

**Supporting Information for**  
**Copper(I)/ABNO-Catalyzed Aerobic Alcohol Oxidation: Alleviating Steric and Electronic Constraints of Cu/TEMPO Catalyst Systems**

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**I. General Considerations.**

$^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker Avance 400 or 500 MHz spectrometer. Chemical shifts ( $\delta$ ) are given in parts per million and are referenced to the residual solvent signal (all  $^{13}\text{C}$  NMR spectra and  $^1\text{H}$  NMR spectra in  $\text{DMSO}-d_6$  or  $\text{D}_2\text{O}$ ) or tetramethylsilane (all  $^1\text{H}$  NMR spectra in  $\text{CDCl}_3$ ).<sup>1</sup> All coupling constants are reported in Hz. High-resolution mass spectra were obtained by the mass spectrometry facility at the University of Wisconsin-Madison. GC analyses were performed using a DB-Wax column installed on a Shimadzu GC-17 with FID. Column chromatography was performed with Silicycle 60 silica gel.

All commercial reagents were purchased from Aldrich and used as received unless otherwise noted. 2,4-dinitrophenylhydrazine was purchased from Aldrich and recrystallized from EtOAc/EtOH prior to use.  $\text{CH}_3\text{CN}$  was taken from a solvent system which passes the solvent through a column of activated molecular sieves, but no precautions to exclude air or water from the solvent or reaction mixtures were taken. Reaction mixtures were monitored by TLC using a UV lamp or  $\text{KMnO}_4$  stain to visualize the plate.

## II. General Method for Screening Reaction Conditions.

**Table S1.** Optimization of Cu/ABNO System for the Oxidation of Cyclohexanemethanol.

entry	Cu salt	ligand	co-catalyst	additive	conversion <sup>a</sup>	yield <sup>a</sup>
1	Cu(MeCN) <sub>4</sub> OTf	bpy	TEMPO	NMI	26	17
2	Cu(MeCN) <sub>4</sub> OTf	bpy	ABNO	NMI	42	30
3	Cu(MeCN) <sub>4</sub> OTf	MeObpy	ABNO	NMI	65	52
4	Cu(MeCN) <sub>4</sub> OTf	MeObpy	ABNO	DMAP	64	50
5	CuBr	MeObpy	ABNO	NMI	58	49
6	CuI	MeObpy	ABNO	NMI	58	48
7	CuBr <sub>2</sub>	MeObpy	ABNO	NMI	8	0
8	Cu(MeCN) <sub>4</sub> OTf	MeObpy	ABNO	NMI	95	76 <sup>b</sup>
9	Cu(MeCN) <sub>4</sub> OTf	MeObpy	ABNO	NMI	97	79 <sup>c</sup>
10	Cu(MeCN) <sub>4</sub> OTf	<b>MeObpy</b>	<b>ABNO</b>	<b>NMI</b>	97	<b>85<sup>c,d</sup></b>
11	Cu(MeCN) <sub>4</sub> OTf	-	ABNO	NMI	65	55 <sup>c,d</sup>
12	Cu(MeCN) <sub>4</sub> OTf	MeObpy	-	NMI	18	9 <sup>c,d</sup>
13	Cu(MeCN) <sub>4</sub> OTf	MeObpy	ABNO	-	87	73 <sup>c,d</sup>
14	Cu(MeCN) <sub>4</sub> OTf	MeObpy	ABNO	NMI	11	11 <sup>c,d,e</sup>
15	Cu(MeCN) <sub>4</sub> OTf	MeObpy	ABNO	NMI	-	57 <sup>d,f,g</sup>
16	Cu(MeCN) <sub>4</sub> OTf	MeObpy	ABNO	NMI	-	51 <sup>d,f,h</sup>
17	Cu(MeCN) <sub>4</sub> OTf	MeObpy	ABNO	NMI	25	18 <sup>i</sup>
18	Cu(MeCN) <sub>4</sub> OTf	MeObpy	ABNO	NMI	70	58 <sup>i,j</sup>

Reactions were performed on a 0.2 mmol scale at 0.2 M substrate in MeCN

<sup>a</sup> Conversion and yield (%) were determined by GC analysis accounting for response factors

<sup>b</sup> 5 mol% Cu(MeCN)<sub>4</sub>OTf, 5 mol% MeObpy, 5 mol% ABNO, 10 mol% NMI

<sup>c</sup> 5 mol% Cu(MeCN)<sub>4</sub>OTf, 5 mol% MeObpy, 1 mol% ABNO, 10 mol% NMI

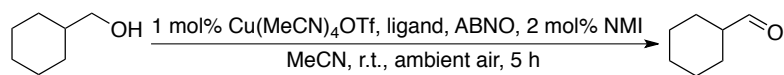
<sup>d</sup> 0.1 M substrate in MeCN. <sup>e</sup> 0.5 mmol scale under N<sub>2</sub>. <sup>f</sup> 1 mmol scale. <sup>g</sup> 50 °C for 24 h.

<sup>h</sup> O<sub>2</sub> balloon for 2.5 h. <sup>i</sup> 1 mol% CyCO<sub>2</sub>H added. <sup>j</sup> Second addition of catalyst after 1.75 h.

### General Procedure for the Screening of Cu/ABNO Reaction Conditions (Table S1)

A solution of Cu(MeCN)<sub>4</sub>OTf and 4,4'-dimethoxy-2,2'-bipyridine (MeObpy) was added to a solution of alcohol (0.2 mmol) in a 13x100mm test tube. A solution of ABNO and a solution of NMI were then added. The reaction was stirred at room temperature (22 °C) open to air for 5 h. The reaction mixture was charged with a known amount of (trimethylphenyl)silane and diluted with 1 mL EtOAc, then filtered through a silica plug. The plug was rinsed with an additional 3 mL EtOAc and an aliquot of filtrate was taken up for GC analysis. Yields given account for response factors.

**Table S2.** Bidentate Ligand Screen for Optimization of the Cu/ABNO-Catalyzed Oxidation of Cyclohexanemethanol.

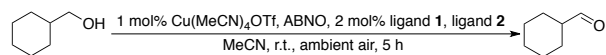




































entry	ligand	yield <sup>a</sup>
1		51
2		2
3		30
4		19
5		1
6		1
7		46
8		1
9		4
10		5
11		4
12		26

Reactions were performed on a 0.2 mmol scale at 0.2 M substrate in MeCN

<sup>a</sup> Yields were determined by GC analysis accounting for response factors

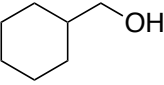
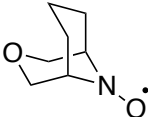
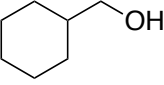
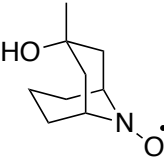
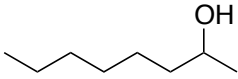
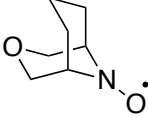
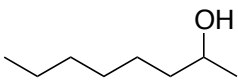
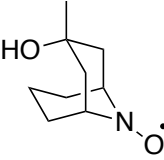
**Table S3.** Monodentate Ligand Screen for the Optimization of the Cu/ABNO-Catalyzed Oxidation of Cyclohexanemethanol.



entry	ligand 1	ligand 2	yield <sup>a</sup>
1			24
2			8
3			6
4			0
5			1
6			37
7			40
8			12
9			1
10			6
11			1
12			13
13			0
14			6
15			0
16			5
17			0

Reactions were performed on a 0.2 mmol scale at 0.2 M substrate in MeCN  
<sup>a</sup> Yields were determined by GC analysis accounting for response factors

**Table S4.** Assessment of novel ABNO derivatives oxidation of cyclohexanemethanol and 2-octanol.

$  \begin{array}{c}  \text{R}^2 \\    \\  \text{R}^1-\text{CH}-\text{OH} \\  \xrightarrow[\text{MeCN, r.t., ambient air, 1 h}]{5 \text{ mol\% Cu(MeCN)}_4\text{OTf, 5 mol\% MeObpy, 1 mol\% ABNO derivative, 10 mol\% NMI}} \\  \text{R}^2 \\    \\  \text{R}^1-\text{C}=\text{O}  \end{array}  $			
entry	substrate	ABNO derivative	yield <sup>a</sup>
1			62
2			83
3			80
4			86

Reactions were performed on a 0.5 mmol scale at 0.1 M substrate in MeCN

<sup>a</sup> Yields were determined by GC analysis accounting for response factors

### III. Method for Gas Uptake Analyses of Cu/Nitroxyl Systems: Comparison of Cu/Nitroxyl Systems in the Oxidation of Cyclohexanemethanol (reactions shown in Figures 1 and 2).

For each reaction, 25 mL round-bottom flasks with stirbars were attached to an apparatus with a calibrated volume and a pressure transducer designed to measure the gas pressure within each of 6 sealed reaction vessels. The apparatus was evacuated and filled with O<sub>2</sub> to 500 torr seven times. The pressure was established at 600 torr and the flasks were heated to 27 °C. Solution A (below) was added via syringe through a septum, then the pressure and temperature were allowed to equilibrate. When the pressure and temperature stabilized, Solution B was added via syringe through a septum. Data were acquired using custom software written within LabVIEW (National Instruments).

# Reaction Conditions for Figure 2 in the Manuscript.

**Table S5.** Solution compositions for gas uptake experiment in Figure 2.

$\text{Cy-CH}_2\text{OH} \xrightarrow[\text{MeCN, 27 } ^\circ\text{C, 600 torr O}_2]{\text{5 mol\% Cu(MeCN)}_4\text{OTf, 5 mol\% bpy, 5 mol\% nitroxyl radical, 10 mol\% NMI}} \text{Cy-CH=O}$		
<div> <div>Cy-CH<sub>2</sub>OH</div> <div>0.4 mmol</div> </div>		
Reaction	Solution A	Solution B
1	cyclohexanemethanol (49.2 μL, 0.4 mmol) in 1.5 mL MeCN	CuOTf (7.54 mg, 0.02 mmol), bpy (3.13 mg, 0.02 mmol), TEMPO (3.13 mg, 0.02 mmol), NMI (3.19 μL, 0.04 mmol) in 500 μL MeCN
2	cyclohexanemethanol (49.2 μL, 0.4 mmol) in 1.5 mL MeCN	CuOTf (7.54 mg, 0.02 mmol), bpy (3.13 mg, 0.02 mmol), ABNO (2.80 mg, 0.02 mmol), NMI (3.19 μL, 0.04 mmol) in 500 μL MeCN
3	cyclohexanemethanol (49.2 μL, 0.4 mmol) in 1.5 mL MeCN	CuOTf (7.54 mg, 0.02 mmol), bpy (3.13 mg, 0.02 mmol), ketoABNO (3.08 mg, 0.02 mmol), NMI (3.19 μL, 0.04 mmol) in 500 μL MeCN
4	cyclohexanemethanol (49.2 μL, 0.4 mmol) in 1.5 mL MeCN	CuOTf (7.54 mg, 0.02 mmol), bpy (3.13 mg, 0.02 mmol), AZADO (3.04 mg, 0.02 mmol), NMI (3.19 μL, 0.04 mmol) in 500 μL MeCN
5	cyclohexanemethanol (49.2 μL, 0.4 mmol) in 1.5 mL MeCN	CuOTf (7.54 mg, 0.02 mmol), bpy (3.13 mg, 0.02 mmol), 4-OMe-TEMPO (3.73 mg, 0.02 mmol), NMI (3.19 μL, 0.04 mmol) in 500 μL MeCN
6	cyclohexanemethanol (49.2 μL, 0.4 mmol) in 1.5 mL MeCN	CuOTf (7.54 mg, 0.02 mmol), bpy (3.13 mg, 0.02 mmol), 4-oxo-TEMPO (3.40 mg, 0.02 mmol), NMI (3.19 μL, 0.04 mmol) in 500 μL MeCN

# Reaction Conditions for Figure 3 in the Manuscript.

**Table S6.** Solution compositions for gas uptake experiment in Figure 3.

$\text{Cy-CH}_2\text{OH} \xrightarrow[\text{MeCN, 27 } ^\circ\text{C, 600 torr O}_2]{\text{5 mol\% Cu(MeCN)}_4\text{OTf, 5 mol\% bpy derivative, 5 mol\% ABNO, 10 mol\% NMI}} \text{Cy-CH=O}$		
0.4 mmol		
Reaction	Solution A	Solution B
1	cyclohexanemethanol (49.2 $\mu\text{L}$ , 0.4 mmol) in 1.5 mL MeCN	CuOTf (7.54 mg, 0.02 mmol), bpy (3.13 mg, 0.02 mmol), ABNO (2.80 mg, 0.02 mmol), NMI (3.19 $\mu\text{L}$ , 0.04 mmol) in 500 $\mu\text{L}$ MeCN
2	cyclohexanemethanol (49.2 $\mu\text{L}$ , 0.4 mmol) in 1.5 mL MeCN	CuOTf (7.54 mg, 0.02 mmol), <sup>MeO</sup> bpy (4.32 mg, 0.02 mmol), ABNO (2.80 mg, 0.02 mmol), NMI (3.19 $\mu\text{L}$ , 0.04 mmol) in 500 $\mu\text{L}$ MeCN
3	cyclohexanemethanol (49.2 $\mu\text{L}$ , 0.4 mmol) in 1.5 mL MeCN	CuOTf (7.54 mg, 0.02 mmol), 4,4'-dimethyl-2,2'-bpy (3.68 mg, 0.02 mmol), ABNO (2.80 mg, 0.02 mmol), NMI (3.19 $\mu\text{L}$ , 0.04 mmol) in 500 $\mu\text{L}$ MeCN
4	cyclohexanemethanol (49.2 $\mu\text{L}$ , 0.4 mmol) in 1.5 mL MeCN	CuOTf (7.54 mg, 0.02 mmol), 4,4'-di( <i>tert</i> -butyl)-2,2'-bpy (5.37 mg, 0.02 mmol), ABNO (2.80 mg, 0.02 mmol), NMI (3.19 $\mu\text{L}$ , 0.04 mmol) in 500 $\mu\text{L}$ MeCN
5	cyclohexanemethanol (49.2 $\mu\text{L}$ , 0.4 mmol) in 1.5 mL MeCN	CuOTf (7.54 mg, 0.02 mmol), 4,4'-di(trifluoromethyl)-2,2'-bpy (3.13 mg, 0.02 mmol), ABNO (2.80 mg, 0.02 mmol), NMI (3.19 $\mu\text{L}$ , 0.04 mmol) in 500 $\mu\text{L}$ MeCN

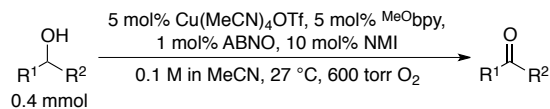
# Reaction Conditions for Figure 4 in the Manuscript.

**Table S7.** Solution compositions for gas uptake experiment in Figure 4A.

$  \begin{array}{c}  \text{OH} \\    \\  \text{R}^1\text{---CH---R}^2 \\  0.4 \text{ mmol}  \end{array}  \xrightarrow[0.2 \text{ M in MeCN, } 27^\circ\text{C, } 600 \text{ torr O}_2]{5 \text{ mol\% Cu(MeCN)}_4\text{OTf, } 5 \text{ mol\% bpy, } 5 \text{ mol\% TEMPO, } 10 \text{ mol\% NMI}}  \begin{array}{c}  \text{O} \\     \\  \text{R}^1\text{---CH---R}^2  \end{array}  $		
Reaction	Solution A	Solution B
1	benzyl alcohol (41.4 $\mu\text{L}$ , 0.4 mmol) in 1.5 mL MeCN	CuOTf (7.54 mg, 0.02 mmol), bpy (3.13 mg, 0.02 mmol), TEMPO (3.13 mg, 0.02 mmol), NMI (3.19 $\mu\text{L}$ , 0.04 mmol) in 500 $\mu\text{L}$ MeCN
2	1-phenylethanol (48.3 $\mu\text{L}$ , 0.4 mmol) in 1.5 mL MeCN	CuOTf (7.54 mg, 0.02 mmol), bpy (3.13 mg, 0.02 mmol), TEMPO (3.13 mg, 0.02 mmol), NMI (3.19 $\mu\text{L}$ , 0.04 mmol) in 500 $\mu\text{L}$ MeCN
3	cyclohexanemethanol (49.2 $\mu\text{L}$ , 0.4 mmol) in 1.5 mL MeCN	CuOTf (7.54 mg, 0.02 mmol), bpy (3.13 mg, 0.02 mmol), TEMPO (3.13 mg, 0.02 mmol), NMI (3.19 $\mu\text{L}$ , 0.04 mmol) in 500 $\mu\text{L}$ MeCN
4	cyclohexanol (40.1 mg, 0.4 mmol) in 1.5 mL MeCN	CuOTf (7.54 mg, 0.02 mmol), bpy (3.13 mg, 0.02 mmol), TEMPO (3.13 mg, 0.02 mmol), NMI (3.19 $\mu\text{L}$ , 0.04 mmol) in 500 $\mu\text{L}$ MeCN
5	N-Boc-DL-norephedrine (100.5 mg, 0.4 mmol) in 1.5 mL MeCN	CuOTf (7.54 mg, 0.02 mmol), bpy (3.13 mg, 0.02 mmol), TEMPO (3.13 mg, 0.02 mmol), NMI (3.19 $\mu\text{L}$ , 0.04 mmol) in 500 $\mu\text{L}$ MeCN



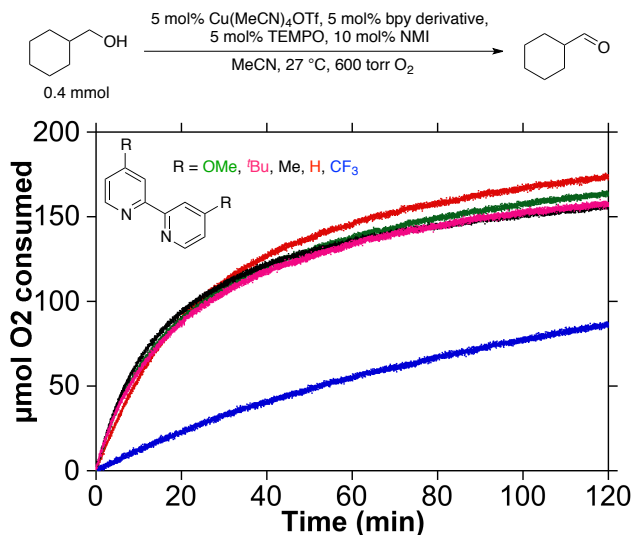
**Table S8.** Solution composition for gas uptake experiment in Figure 4B.



Reaction	Solution A	Solution B
1	benzyl alcohol (41.4 $\mu\text{L}$ , 0.4 mmol) in 3.5 mL MeCN	CuOTf (7.54 mg, 0.02 mmol), <sup>MeO</sup> i <b>bpy</b> (4.32 mg, 0.02 mmol), ABNO (0.56 mg, 0.02 mmol), NMI (3.19 $\mu\text{L}$ , 0.04 mmol) in 500 $\mu\text{L}$ MeCN
2	1-phenylethanol (48.3 $\mu\text{L}$ , 0.4 mmol) in 3.5 mL MeCN	CuOTf (7.54 mg, 0.02 mmol), <sup>MeO</sup> i <b>bpy</b> (4.32 mg, 0.02 mmol), ABNO (0.56 mg, 0.02 mmol), NMI (3.19 $\mu\text{L}$ , 0.04 mmol) in 500 $\mu\text{L}$ MeCN
3	cyclohexanemethanol (49.2 $\mu\text{L}$ , 0.4 mmol) in 3.5 mL MeCN	CuOTf (7.54 mg, 0.02 mmol), <sup>MeO</sup> i <b>bpy</b> (4.32 mg, 0.02 mmol), ABNO (0.56 mg, 0.02 mmol), NMI (3.19 $\mu\text{L}$ , 0.04 mmol) in 500 $\mu\text{L}$ MeCN
4	cyclohexanol (40.1 mg, 0.4 mmol) in 3.5 mL MeCN	CuOTf (7.54 mg, 0.02 mmol), <sup>MeO</sup> i <b>bpy</b> (4.32 mg, 0.02 mmol), ABNO (0.56 mg, 0.02 mmol), NMI (3.19 $\mu\text{L}$ , 0.04 mmol) in 500 $\mu\text{L}$ MeCN
5	N-Boc-DL-norephedrine (100.5 mg, 0.4 mmol) in 3.5 mL MeCN	CuOTf (7.54 mg, 0.02 mmol), <sup>MeO</sup> i <b>bpy</b> (4.32 mg, 0.02 mmol), ABNO (0.56 mg, 0.02 mmol), NMI (3.19 $\mu\text{L}$ , 0.04 mmol) in 500 $\mu\text{L}$ MeCN

## Additional Experiments.

**Figure S1.** Oxidation of cyclohexanemethanol with bpy derivatives using TEMPO as a nitroxyl cocatalyst.

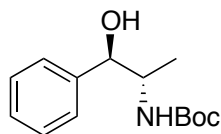


**Table S9.** Solution composition for gas uptake experiment in Figure S1.

Reaction	Solution A	Solution B
1	cyclohexanemethanol (49.2 $\mu\text{L}$ , 0.4 mmol) in 1.5 mL MeCN	CuOTf (7.54 mg, 0.02 mmol), MeObpy (4.32 mg, 0.02 mmol), TEMPO (3.13 mg, 0.02 mmol), NMI (3.19 $\mu\text{L}$ , 0.04 mmol) in 500 $\mu\text{L}$ MeCN
2	cyclohexanemethanol (49.2 $\mu\text{L}$ , 0.4 mmol) in 1.5 mL MeCN	CuOTf (7.54 mg, 0.02 mmol), 4,4'- <i>tert</i> -butyl-2,2'-bpy (5.37 mg, 0.02 mmol), TEMPO (3.13 mg, 0.02 mmol), NMI (3.19 $\mu\text{L}$ , 0.04 mmol) in 500 $\mu\text{L}$ MeCN
3	cyclohexanemethanol (49.2 $\mu\text{L}$ , 0.4 mmol) in 1.5 mL MeCN	CuOTf (7.54 mg, 0.02 mmol), 4,4'-dimethyl-2,2'-bpy (3.68 mg, 0.02 mmol), TEMPO (3.13 mg, 0.02 mmol), NMI (3.19 $\mu\text{L}$ , 0.04 mmol) in 500 $\mu\text{L}$ MeCN
4	cyclohexanemethanol (49.2 $\mu\text{L}$ , 0.4 mmol) in 1.5 mL MeCN	CuOTf (7.54 mg, 0.02 mmol), bpy (3.13 mg, 0.02 mmol), TEMPO (3.13 mg, 0.02 mmol), NMI (3.19 $\mu\text{L}$ , 0.04 mmol) in 500 $\mu\text{L}$ MeCN
5	cyclohexanemethanol (49.2 $\mu\text{L}$ , 0.4 mmol) in 1.5 mL MeCN	CuOTf (7.54 mg, 0.02 mmol), 4,4'-di(trifluoromethyl)-2,2'-bpy (5.84 mg, 0.02 mmol), TEMPO (3.13 mg, 0.02 mmol), NMI (3.19 $\mu\text{L}$ , 0.04 mmol) in 500 $\mu\text{L}$ MeCN

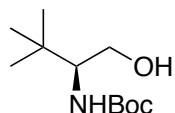
#### IV. Synthesis and Characterization of Substrates.

##### Representative Procedure for the Synthesis of Boc-Protected Aminoalcohols.



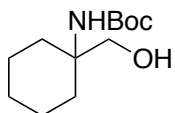
##### ***N*-Boc-LD-norephedrine.**

Boc<sub>2</sub>O (3.32 g, 15.2 mmol, 1.15 equiv) was added to a stirred solution of norephedrine (2.00 g, 13.2 mmol, 1 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (55 mL) under N<sub>2</sub> at 0 °C. NEt<sub>3</sub> (2.30 mL, 13.2 mmol, 1 equiv) was then added dropwise via syringe. The resulting colorless solution was slowly warmed to r.t. and stirred for 48 h. At this point, the reaction was neutralized with aq. citric acid and the organic layer was washed with sat. aq. NaHCO<sub>3</sub>, H<sub>2</sub>O, then brine. The organic extracts were dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo. The crude material was purified by silica column chromatography (20-40% EtOAc/hexanes gradient elution) to yield the product as a white solid (3.05 g, 92 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.39 – 7.22 (m, 5H), 4.84 (dd, *J* = 3.6, 3.6 Hz, 1H), 4.66 (d, *J* = 8 Hz, 1H), 4.00 (s, 1H), 3.30 (s, 1H), 1.46 (s, 9H), 0.98 (d, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 156.39, 140.85, 128.14, 127.44, 126.35, 79.80, 76.80, 52.03, 28.42, 14.82. Spectral properties are consistent with literature values.<sup>2</sup>



##### ***N*-Boc-*tert*-leucinol.**

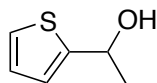
The crude material was purified by silica column chromatography (20-100% EtOAc/hexanes gradient elution). A white solid (1.23 g, 86 %) was isolated. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 4.67 (d, *J* = 8.0 Hz, 1H), 3.91 – 3.70 (m, 1H), 3.52 – 3.45 (m, 2H), 2.38 – 2.35 (m, 1H), 1.46 (s, 9H), 0.94 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 157.21, 79.59, 63.20, 61.03, 33.67, 28.39, 26.82. Spectral properties are consistent with literature values.<sup>3</sup>



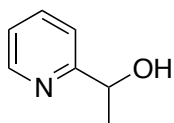
##### **1-[1-(*tert*-butoxycarbonylamino)cyclohexyl]methanol.**

The crude material was purified by silica column chromatography (30-100% EtOAc/hexanes gradient elution). A white crystalline solid (1.59 g, 75 %) was isolated. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 6.02 (s, 1H), 4.54 (t, *J* = 5.7 Hz, 1H), 3.37 (d, *J* = 5.8 Hz, 2H), 1.92 (d, *J* = 13.0 Hz, 2H), 1.54 – 1.13 (m, 8H), 1.39 (s, 9H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 155.34, 78.00, 66.79, 56.28, 31.34, 29.23, 26.33, 22.01. Spectral properties are consistent with literature values.<sup>4</sup>

## Representative Procedure for the Synthesis $\alpha$ -Methyl Heteroaromatic Alcohols



A solution of MeMgBr (4.20 mL, 1.8M, 7.50 mmol, 3 equiv) was added dropwise via syringe to a solution of the 2-thiophenecarboxaldehyde (234  $\mu$ L, 2.50 mmol, 1 equiv) in Et<sub>2</sub>O (12 mL) at 0 °C under N<sub>2</sub>. The resulting light yellow solution was stirred for 2 h between 0 and 5 °C, then quenched with sat. aq. NH<sub>4</sub>Cl and extracted with Et<sub>2</sub>O (3 x 30 mL). The organic layers were combined, dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo, yielding a yellow oil (242 mg, 76 %) consistent with the desired product. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.23 (dd,  $J$  = 4.7, 1.6 Hz, 1H), 6.99 – 6.93 (m, 2H), 5.18 – 5.06 (m, 1H), 2.19 – 2.10 (m, 1H), 1.59 (d,  $J$  = 6.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  149.89, 126.68, 124.45, 123.22, 66.27, 25.29. Spectral properties are consistent with literature values.<sup>5</sup>



### 2-(1-hydroxyethyl)pyridine.

The crude material was purified by silica column chromatography (30-50% EtOAc/hexanes gradient elution, 5% v/v NEt<sub>3</sub> added to eluent). A clear oil (187 mg, 61 %) was isolated. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.54 (d,  $J$  = 5.1 Hz, 1H), 7.69 (td,  $J$  = 7.7, 1.7 Hz, 1H), 7.28 (d,  $J$  = 7.7 Hz, 1H), 7.20 (dd,  $J$  = 7.2, 5.1 Hz, 1H), 4.89 (dt,  $J$  = 9.5, 5.1 Hz, 1H), 4.31 (s, 1H), 1.51 (d,  $J$  = 6.6 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  163.00, 148.14, 136.80, 122.23, 119.81, 68.81, 24.29. Spectral properties are consistent with literature values.<sup>6</sup>

## V. Oxidation of Primary and Secondary Alcohols.

All alcohols except those described in Section IV were obtained from commercial sources and used as received. 2,2-Dimethyl-1-phenyl-1-propanol and 1-adamantanemethanol were purified by silica column chromatography prior to use. Aldehyde products were isolated or trapped using 2,4-dinitrophenylhydrazine, and the <sup>1</sup>H and <sup>13</sup>C NMR spectra were compared to literature values. For those not available in the literature, full characterization is provided below.

### Representative Procedure for the Oxidation of Primary and Secondary Alcohols.

Solid Cu(MeCN)<sub>4</sub>OTf (18.8 mg, 0.05 mmol, 0.05 equiv), 4,4'-dimethoxy-2,2'-bipyridine (<sup>MeO</sup>bpy) (10.8 mg, 0.05 mmol, 0.05 equiv), ABNO (1.4 mg, 0.01 mmol, 0.01 equiv), and NMI (8.0  $\mu$ L, 0.1 mmol, 0.1 equiv) were added to a solution of alcohol (1 mmol) in MeCN (1 mL) in a 25x150 mm test tube with an oval (0.625 x 0.25 in) stirbar. The addition of each catalytic component was followed by a rinse of MeCN (1 mL). The reaction volume was diluted to 10 mL with MeCN and the dark red/brown solution was stirred at 950 RPM open to air at room temperature until no starting material remained by TLC analysis. Reaction completion is often accompanied by a change in color to blue or

green. Preliminary experiments indicate that stir rate impacts the rate of reaction; however, the order of addition of reaction components does not affect product yield.



$(^{\text{MeO}}\text{bpy})\text{Cu}^{\text{I}}/\text{ABNO}/\text{NMI}$ -catalyzed alcohol oxidation stirring at 950 RPM

10 mmol reactions were run in 500 mL round-bottom flasks with 24/40 neck:

10 mmol reactions of 2-octanol, Boc-L-valinol, and cyclohexanemethanol were run in 100 mL MeCN and stirred at 950 RPM with an oval (1 x 0.5 in) stirbar.

The 50 mmol reaction was run in a 1 L round-bottom flask with 24/40 neck:

The 50 mmol reaction of 1-Boc-3-hydroxyazetidine was run in 250 mL MeCN and stirred at 950 RPM with an oval (1 x 0.5 in) stirbar.

#### *Purification Method A.*

Upon completion of the reaction (based on TLC analysis), the reaction mixture was diluted with Et<sub>2</sub>O (20 mL) and filtered through a 1 cm silica plug. The plug was rinsed with Et<sub>2</sub>O (100 mL) and the filtrate was concentrated in vacuo to yield the aldehyde or ketone that was pure by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies. Residual ABNO is evident by GC analysis and can be removed by silica column chromatography.

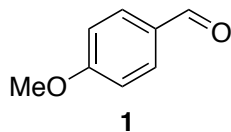
#### *Purification Method B (for some volatile aldehydes and ketones).*

Upon completion of the reaction, based on TLC analysis, the reaction mixture was quenched with the addition of H<sub>2</sub>O (30 mL). The aqueous layer was extracted with pentane (3 x 30 mL). The organic layers were combined, washed with brine, dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo at 0 °C to afford the product as a slightly colored oil that was pure by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies or isolated as a solution in pentane. Residual ABNO is evident by GC analysis and can be removed by silica column chromatography.

#### *Isolation of volatile aldehydes and ketones.*

Some 1 mmol reactions forming volatile aldehydes were subjected to treatment with H<sub>2</sub>O (4 mL), HCl (500 μL, 6M aq.), then 2,4-dinitrophenylhydrazine (204 mg, 1.03 mmol, 1.03 equiv) upon completion. Reactions were stirred for an additional hour and monitored by TLC. Successful hydrazone formation is often accompanied by formation of a bright yellow to red precipitate. Isolation of the hydrazone is substrate-dependent and described in Section VI.

## VI. Characterization of Aldehyde and Ketone Products.

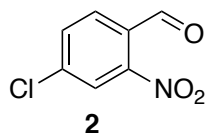


### 4-methoxybenzaldehyde.

The reaction was run in a 25x150 mm test tube under air at room temperature for 1 h. The reaction mixture was purified according to *Method A*, yielding the title compound as a slightly colored oil (132 mg, 97 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.89 (s, 1H), 7.84 (d,  $J$  = 8.6 Hz, 2H), 7.01 (d,  $J$  = 8.6 Hz, 2H), 3.90 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  190.83, 164.62, 132.00, 129.97, 114.33, 55.61. Spectral properties are consistent with literature values.<sup>7</sup>

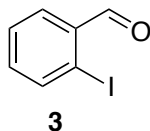
Reaction (1 mmol) with 1 mol%  $\text{Cu}(\text{MeCN})_4\text{OTf}$ , 1 mol%  $^{\text{MeO}}\text{bpy}$ , 1 mol% ABNO, 2 mol% NMI:

The reaction was performed in a 25x150 mm test tube under air at room temperature for 20 h. The reaction mixture was purified according to *Method A*, yielding a yellow solid (147 mg) that was confirmed to be a mixture of the desired product (61 %) and starting material (39 %) by  $^1\text{H}$  NMR spectroscopy.



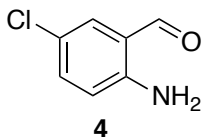
### 4-chloro-2-nitrobenzaldehyde.

The reaction was run on a 2 mmol scale in a 100mL round-bottom flask with 24/40 neck under air at 50 °C for 2.2 h. The reaction mixture was purified according to *Method A*, yielding the title compound as a light yellow solid (358 mg, 96 %) with 1.5 % RSM by  $^1\text{H}$  NMR spectroscopy.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.39 (s, 1H), 8.11 (d,  $J$  = 2.0 Hz, 1H), 7.95 (d,  $J$  = 8.3 Hz, 1H), 7.77 (dd,  $J$  = 8.3, 1.2 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  187.05, 150.25, 140.42, 134.39, 131.12, 129.50, 125.00. Spectral properties are consistent with literature values.<sup>8</sup>



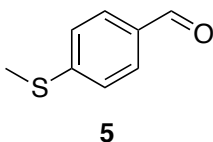
### 2-iodobenzaldehyde.

The reaction was run in a 25x150 mm test tube under air at room temperature for 1 h. The reaction mixture was purified according to *Method A*, yielding the title compound as a yellow oil (227 mg, 98 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.07 (s, 1H), 7.96 (d,  $J$  = 7.9 Hz, 1H), 7.89 (d,  $J$  = 7.7 Hz, 1H), 7.47 (t,  $J$  = 7.4 Hz, 1H), 7.29 (t,  $J$  = 7.7 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.79, 140.67, 135.50, 135.14, 130.28, 128.74, 100.73. Spectral properties are consistent with literature values.<sup>7</sup>



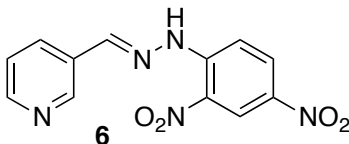
**2-amino-5-chlorobenzaldehyde.**

The reaction was run in a 25x150 mm test tube under air at room temperature for 1 h. The reaction mixture was purified according to *Method A*, yielding the title compound as a yellow solid (150 mg, 97 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.81 (s, 1H), 7.45 (d, *J* = 2.6 Hz, 1H), 7.26 (dd, *J* = 8.8, 4 Hz, 1H), 6.62 (d, *J* = 8.8 Hz, 1H), 6.13 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 192.85, 148.35, 135.28, 134.32, 120.79, 119.31, 117.68. Spectral properties are consistent with literature values.<sup>9</sup>



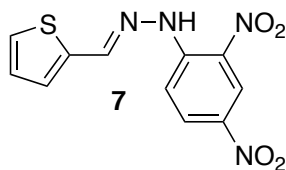
**4-(thiomethyl)benzaldehyde.**

The reaction was run in a 25x150 mm test tube under air at room temperature for 1 h. The reaction mixture was purified according to *Method B* using Et<sub>2</sub>O as the organic layer, yielding the title compound as a yellow oil (146 mg, 96 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.92 (s, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 2.53 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 191.26, 147.93, 132.95, 130.01, 125.19, 14.71. Spectral properties are consistent with literature values.<sup>10</sup>



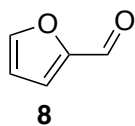
**3-pyridinecarboxaldehyde-(2,4-dinitrophenylhydrazone).**

The reaction was run in a 25x150 mm test tube under air at room temperature for 1 h. Upon completion by TLC, the blue solution was treated with H<sub>2</sub>O (4 mL), HCl (500 μL, 6M aq.), then 2,4-dinitrophenylhydrazine (204 mg, 1.03 mmol, 1.03 equiv). Formation of the hydrazone was indicated by appearance of a bright yellow precipitate. After 1 h, the reaction was complete by TLC. The slurry was filtered, washed with cold H<sub>2</sub>O, and air-dried, affording the title compound as a yellow solid (253 mg, 88 %). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 11.90 (s, 1H), 9.14 (s, 1H), 8.90 (d, *J* = 2.7 Hz, 1H), 8.81 (s, 2H), 8.59 (d, *J* = 8.2 Hz, 1H), 8.42 (dd, *J* = 9.4, 2.6 Hz, 1H), 8.23 (d, *J* = 9.6 Hz, 1H), 7.84 (dd, *J* = 8.1, 5.1 Hz, 1H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 148.02, 146.13, 145.34, 144.68, 138.19, 137.69, 131.75, 130.67, 130.19, 125.86, 123.34, 117.58. HRMS (ESI) [M+H]<sup>+</sup>/*z* calcd. 288.0728, found 288.0714.



### 2-thiophenecarboxaldehyde-(2,4-dinitrophenylhydrazone).

The reaction was run in a 25x150 mm test tube under air at room temperature for 1 h. Upon completion by TLC, the blue solution was treated with H<sub>2</sub>O (4 mL), HCl (500 µL, 6M aq.), then 2,4-dinitrophenylhydrazine (204 mg, 1.03 mmol, 1.03 equiv). Formation of the hydrazone was indicated by appearance of a bright red precipitate. After 1 h, the reaction was complete by TLC. The slurry was diluted with H<sub>2</sub>O (100 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 100 mL). The organic layers were combined, dried over MgSO<sub>4</sub>, and concentrated in vacuo. The resulting red solid was re-dissolved in CH<sub>2</sub>Cl<sub>2</sub>, filtered through a plug of silica (1 cm) to remove excess hydrazine, and rinsed with CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was concentrated in vacuo, affording the title compound as a red solid (293 mg, >98 %). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 11.69 (s, 1H), 8.93 (s, 1H), 8.87 (d, *J* = 2.6 Hz, 1H), 8.43 (dd, *J* = 9.6, 2.7 Hz, 1H), 7.92 (d, *J* = 9.6 Hz, 1H), 7.76 (d, *J* = 5.0 Hz, 1H), 7.52 (d, *J* = 3.6 Hz, 1H), 7.19 (dd, *J* = 5.0, 3.6 Hz, 1H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 144.97, 144.93, 138.98, 137.20, 132.13, 130.28, 130.24, 129.98, 128.71, 123.58, 116.86. HRMS (ESI) [2M + NH<sub>4</sub>]<sup>+</sup>/*z* calcd. 602.0871, found 602.0859.



### 2-furfural.

The reaction was run in a 25x150 mm test tube under air at room temperature for 1 h. The reaction mixture was purified according to *Method B*, yielding the title compound as a solution in pentane (157 mg total, pentane accounts for 42% total sample mass. See calculation guideline below). The product is a clear oil (91 mg, 95 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.68 (s, 1H), 7.69 (s, 1H), 7.25 (s, 1H), 6.60 (dd, *J* = 3.6, 1.6 Hz, 1H). Spectral properties are consistent with literature values.<sup>7</sup>

Method for yield determination for products obtained as a solution in pentane:

$$\frac{\frac{\text{solvent integration}}{\# \text{ hydrogen atoms}}}{\left(\frac{\text{product integration}}{\# \text{ hydrogen atoms}}\right) + \left(\frac{\text{solvent integration}}{\# \text{ hydrogen atoms}}\right)} = \text{mol \% solvent}$$

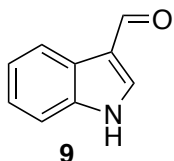
$$\left(\frac{\text{product integration}}{\# \text{ hydrogen atoms}}\right)(\text{product molecular weight}) + \left(\frac{\text{mol \% solvent}}{100}\right)(\text{solvent molecular weight}) = \text{total relative mass}$$

$$\left(\frac{\left(\frac{\text{mol \% solvent}}{100}\right)(\text{solvent molecular weight})}{\text{total relative mass}}\right)(100) = \text{mass \% solvent}$$



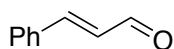
$$(\text{total mass of sample}) \left( \frac{\text{mass \% solvent}}{100} \right) = \text{mg solvent in sample}$$

$$\text{total mass of sample} - \text{mass of solvent in sample} = \text{total mass of desired product}$$



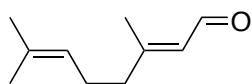
**indole-3-carboxaldehyde.**

The reaction was run in a 25x150 mm test tube under air at room temperature for 3 h. The reaction mixture was purified by silica column chromatography (50-100% EtOAc/hexanes gradient elution, 5% v/v NEt<sub>3</sub> added to eluent), yielding the title compound as a yellow solid (124 mg, 86 %) with 4.3% RSM by <sup>1</sup>H NMR spectroscopy. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 12.15 (s, 1H), 9.95 (s, 1H), 8.31 (s, 1H), 8.11 (d, *J* = 6.9 Hz, 1H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.28 (dt, *J* = 7.2, 1.3 Hz, 1H), 7.24 (dt, *J* = 7.2, 1.3 Hz, 1H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 185.43, 138.94, 137.51, 124.58, 123.93, 122.59, 121.29, 118.63, 112.89. Spectral properties are consistent with commercially available product.



**trans-cinnamaldehyde.**

The reaction was run in a 25x150 mm test tube under air at room temperature for 1 h. The reaction mixture was purified according to *Method B*, yielding the title compound as a light yellow oil (125 mg, 95 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.71 (d, *J* = 7.7 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.53 – 7.40 (m, 4H), 6.73 (dd, *J* = 16.0, 7.7 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 193.74, 152.83, 134.03, 131.32, 129.14, 128.64, 128.52. Spectral properties are consistent with literature values.<sup>7</sup>



**citral.**

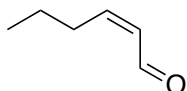
The reaction was run in a 25x150 mm test tube under air at room temperature for 1 h. The reaction mixture was purified according to *Method B*, yielding the title compound as a clear oil (147 mg, 97 %). 98:2 E:Z by <sup>1</sup>H NMR spectroscopy. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.00 (d, *J* = 8.1 Hz, 1H), 5.89 (d, *J* = 8.1 Hz, 1H), 5.10 – 5.05 (m, 1H), 2.29 – 2.12 (m, 7H), 1.69 (s, 3H), 1.61 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 191.33, 163.86, 132.95, 127.44, 122.57, 40.63, 25.75, 25.68, 17.74, 17.61. Spectral properties are consistent with literature values.<sup>7</sup>



**12**

### 3-phenyl-2-propynal.

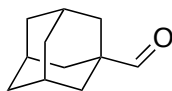
The reaction was run in a 25x150 mm test tube under an O<sub>2</sub> balloon at room temperature for 1 h. The reaction mixture was purified according to *Method B*, yielding the title compound as a yellow oil (110 mg, 85 %) with 2.5% RSM by <sup>1</sup>H NMR spectroscopy. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.43 (s, 1H), 7.63 – 7.58 (m, 2H), 7.53 – 7.28 (m, 3H). Spectral properties are consistent with literature values.<sup>7</sup>



**13**

### cis-hexenal.

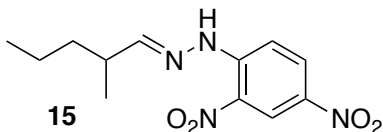
The sample of *cis*-2-hexen-1-ol used in this experiment was >19:1 Z:E by <sup>1</sup>H NMR spectroscopy. The reaction was run in a 25x150 mm test tube under air at room temperature for 1 h. The reaction mixture was purified according to *Method B*, yielding the title compound as a solution in pentane. The product is a clear oil (97 mg, >98 %) that is >19:1 Z:E by <sup>1</sup>H NMR spectroscopy (yield determination was performed similar to that of furfural **8** - see above). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.09 (d, *J* = 8.1 Hz, 1H), 6.63 (dt, *J* = 11.2, 8.1 Hz, 1H), 5.98 (ddt, *J* = 11.2, 8.1, 1.6 Hz, 1H), 2.63–2.56 (m, 2H), 1.57–1.53 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 190.93, 153.14, 130.39, 29.87, 22.41, 13.55. Spectral properties are consistent with literature values.<sup>7</sup>



**14**

### 1-adamantanecarboxaldehyde.

The reaction was run in a 25x150 mm test tube under air at room temperature for 1 h. The reaction mixture was purified according to *Method A*, yielding the title compound as a white solid (152 mg, 92 %) with 2.0% RSM by <sup>1</sup>H NMR spectroscopy. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.32 (s, 1H), 2.08 (s, 2H), 1.84 – 1.65 (m, 13H). Spectral properties are consistent with literature values.<sup>11</sup>

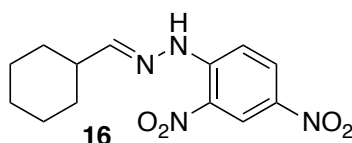


**15**

### 2-methyl-1-pentanal-(2,4-dinitrophenylhydrazone).

The reaction was run in a 25x150 mm test tube under air at room temperature for 1 h. Upon completion by TLC, the blue solution was treated with H<sub>2</sub>O (4 mL), HCl (500 μL, 6M aq.), then 2,4-dinitrophenylhydrazine (204 mg, 1.03 mmol, 1.03 equiv). Formation

of the hydrazone was indicated by appearance of a bright yellow precipitate. After 1 h, the reaction was complete by TLC. The slurry was diluted with H<sub>2</sub>O (40 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 40 mL). The organic layers were combined, dried over MgSO<sub>4</sub>, and concentrated in vacuo. The resulting yellow solid was re-dissolved in CH<sub>2</sub>Cl<sub>2</sub>, filtered through a plug of silica (1 cm) to remove excess hydrazine, and rinsed with CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was concentrated in vacuo, affording the title compound as a yellow solid (264 mg, 94 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.98 (s, 1H), 9.12 (d, *J* = 2.6 Hz, 1H), 8.30 (dd, *J* = 9.6, 2.6 Hz, 1H), 7.92 (d, *J* = 9.6 Hz, 1H), 7.42 (d, *J* = 5.9 Hz, 1H), 2.63–2.53 (m, 1H), 1.66 – 1.30 (m, 4H), 1.18 (d, *J* = 6.8 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 156.91, 145.24, 137.76, 129.96, 128.83, 123.52, 116.57, 36.71, 36.57, 20.26, 17.64, 14.06. HRMS (ESI) [2M + NH<sub>4</sub>]<sup>+</sup>/*z* calcd. 578.2682, found 278.2686.

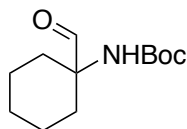


**cyclohexanecarboxaldehyde-(2,4-dinitrophenylhydrazone).**

The reaction was run in a 25x150 mm test tube under air at room temperature for 1 h. Upon completion by TLC, the blue solution was treated with H<sub>2</sub>O (4 mL), HCl (500 μL, 6M aq.), then 2,4-dinitrophenylhydrazine (204 mg, 1.03 mmol, 1.03 equiv). Formation of the hydrazone was indicated by appearance of a bright yellow precipitate. After 1 h, the reaction was complete by TLC. The slurry was diluted with H<sub>2</sub>O (40 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 40 mL). The organic layers were combined, dried over MgSO<sub>4</sub>, and concentrated in vacuo. The resulting yellow solid was re-dissolved in CH<sub>2</sub>Cl<sub>2</sub>, filtered through a plug of silica (1 cm) to remove excess hydrazine, and rinsed with CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was concentrated in vacuo, affording the title compound as a yellow solid (296 mg, >98 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 10.97 (s, 1H), 9.12 (d, *J* = 2.6 Hz, 1H), 8.29 (dd, *J* = 9.6, 2.6 Hz, 1H), 7.92 (d, *J* = 9.6 Hz, 1H), 7.44 (d, *J* = 5.2 Hz, 1H), 2.48 – 2.34 (m, 1H), 1.98 – 1.77 (m, 4H), 1.77 – 1.67 (m, 1H), 1.44 – 1.18 (m, 5H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 156.31, 145.24, 137.68, 129.93, 128.76, 123.54, 116.53, 40.93, 30.03, 25.84, 25.40. HRMS (ESI) [2M + NH<sub>4</sub>]<sup>+</sup>/*z* calcd. 602.2682, found 602.2667.

10 mmol scale reaction:

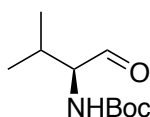
The reaction was run in a 500 mL round-bottom flask open to air with 1 x 0.5-inch oval stirbar. After 1 h, the reaction was complete by TLC and hydrazone formation protocol was followed as performed above. A yellow solid (2.83 g, 97 %) was isolated and consistent with the desired product by <sup>1</sup>H NMR spectroscopy.



17

**1-(Boc)amino-1-formylcyclohexane.**

The reaction was run in a 25x150 mm test tube under air at room temperature for 1 h. The reaction mixture was purified according to *Method B* using Et<sub>2</sub>O as the organic layer, yielding the title compound as a light yellow oil (204 mg, 90 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.49 (s, 1H), 4.86 (s, 1H), 1.76 – 1.65 (m, 7H), 1.44 (s, 9H), 1.37 – 1.22 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 201.93, 154.80, 80.29, 61.47, 29.68, 28.27, 25.05, 20.96. HRMS (ESI) [M+H]<sup>+</sup>/z calcd. 228.1595, found 228.1598.



18

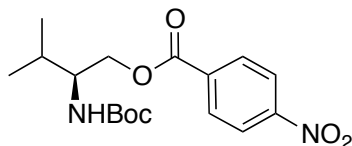
**N-Boc-L-valinal.**

The reaction was run in a 25x150 mm test tube under air at room temperature for 1 h. The reaction mixture was purified according to *Method B* using Et<sub>2</sub>O as the organic layer, yielding the title compound as a slightly colored oil (201 mg, >98 %). Isolated as a mixture of Boc rotamers. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.65 (s, 1H), 5.10 (s, 1H), 4.25 (dd, *J* = 7.9, 4.3 Hz, 1H), 2.35 – 2.18 (m, 1H), 1.45 (s, 9H), 1.03 (d, *J* = 6.9 Hz, 3H), 0.95 (d, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 200.38, 155.85, 79.97, 64.67, 29.08, 28.29, 19.06, 17.58. 98 % ee based on HPLC analysis. Analysis of % ee is shown in the HPLC traces of (*R*)-2-((Boc)amino)-3-methylbutyl-4-nitrobenzoate below. Spectral properties are consistent with literature values.<sup>12</sup>

Note: Attempting to employ purification *Method A* or perform silica column chromatography to isolate this α-aminoaldehyde will result in epimerization of the stereocenter. In addition, the α-aminoaldehyde will epimerize upon standing under ambient conditions. Thus, further derivatization should be performed in situ (ideally) or immediately following product isolation.

10 mmol scale reaction:

The reaction was run in a 500 mL round-bottom flask open to air with a 1 x 0.5-inch stirbar. After 1 h, the reaction was complete by TLC and was concentrated in vacuo. The blue residue was then diluted with H<sub>2</sub>O (300 mL) and extracted with EtOAc (3 x 300 mL). The organic layers were combined, washed with brine, dried over MgSO<sub>4</sub>, and concentrated in vacuo. A yellow oil (1.81 g, 90 %) was isolated and confirmed to be the desired product by <sup>1</sup>H NMR spectroscopy. Lower enantiopurity of the isolated product (77 % ee, based on HPLC analysis of (*R*)-2-((Boc)amino)-3-methylbutyl-4-nitrobenzoate; see HPLC trace below) relative to the 1 mmol scale reactions is attributed to the longer time required for product isolation steps.

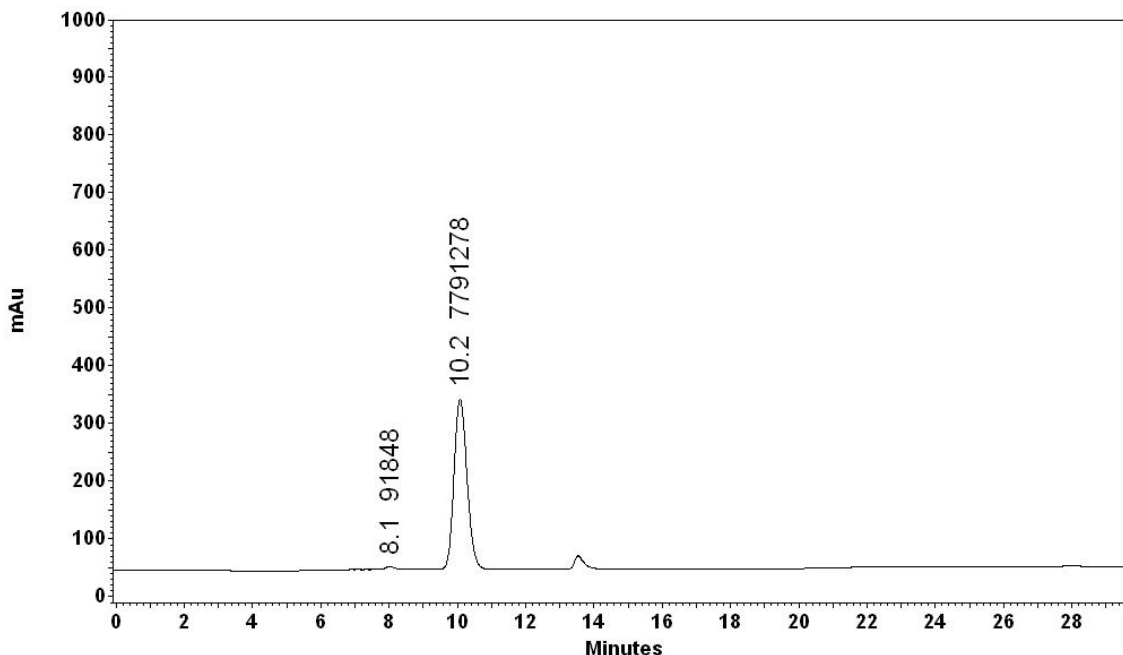


**(*R*)-2-((Boc)amino)-3-methylbutyl-4-nitrobenzoate.**

*N*-Boc-L-valinal (50 mg, 0.25 mmol, 1 equiv) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) and treated with NaBH<sub>4</sub> (150 mg, 3.96 mmol, 15.8 equiv). Upon completion of the reduction by TLC, the reaction mixture was quenched with the dropwise addition of sat. aq. NH<sub>4</sub>Cl and extracted with EtOAc (3 x 30 mL). The organic layers were combined, dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo, yielding a yellow solid that was then redissolved in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) under N<sub>2</sub>. NEt<sub>3</sub> (70  $\mu$ L, 0.5 mmol, 2 equiv) was added, followed by 4-nitrobenzoyl chloride (56 mg, 0.3 mmol, 1.2 equiv). The resulting yellow solution was stirred for 16 h at room temperature, then quenched with sat. aq. NH<sub>4</sub>Cl and extracted with EtOAc (3 x 30 mL). The organic layers were combined, washed with brine, dried over MgSO<sub>4</sub>, and concentrated in vacuo, yielding the title compound as a yellow solid (58 mg, 66 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.35 – 8.14 (m, 4H), 4.54 (d, *J* = 9.9 Hz, 1H), 4.48 – 4.25 (m, 2H), 3.93 – 3.86 (m, 1H), 1.93 – 1.84 (m, 1H), 1.40 (s, 9H), 1.03 (d, *J* = 6.6 Hz, 3H), 1.00 (d, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  164.69, 155.77, 150.62, 135.42, 130.86, 123.54, 79.56, 66.63, 54.54, 29.80, 28.39, 28.34, 19.43, 18.30. HRMS (ESI) [M+H]<sup>+</sup>/*z* calcd. 353.1708, found 353.1700.

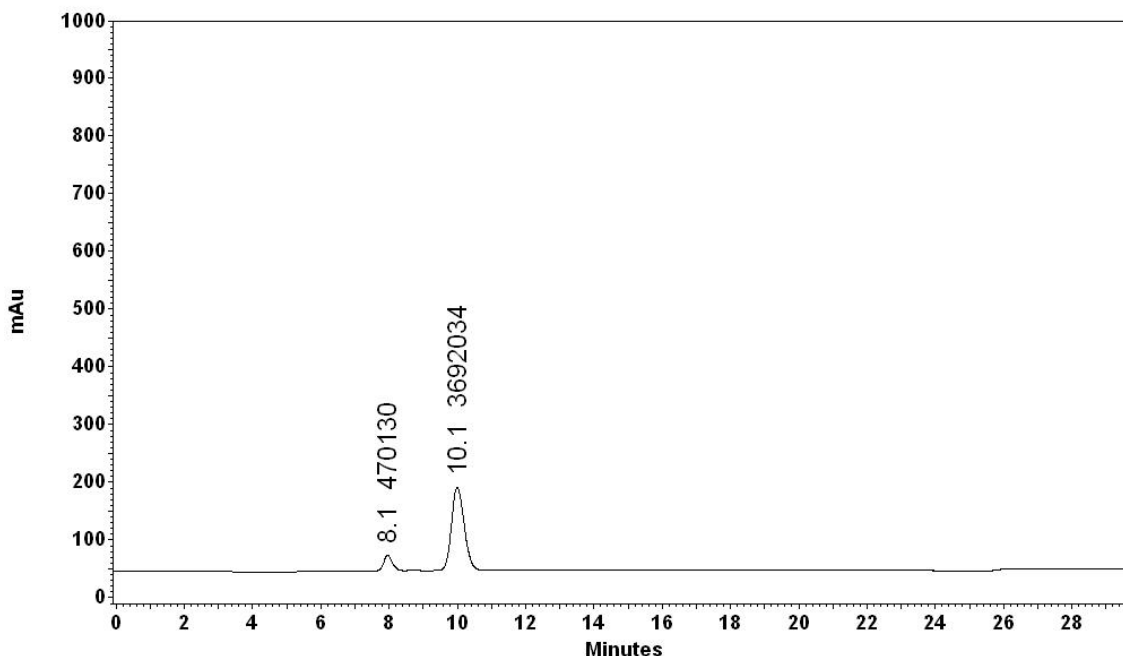
Analysis of (*R*)-2-((Boc)amino)-3-methylbutyl-4-nitrobenzoate from 1 mmol scale oxidation of *N*-Boc-L-valinol.

Chiralcel AS-*H*, 5-25% iPrOH, 1 mL/min, 254 nm, 98 % ee



Analysis of (*R*)-2-((Boc)amino)-3-methylbutyl-4-nitrobenzoate from 10 mmol scale oxidation of *N*-Boc-L-valinol.

Chiralcel AS-*H*, 5-25% iPrOH, 1 mL/min, 254 nm, 77 % ee



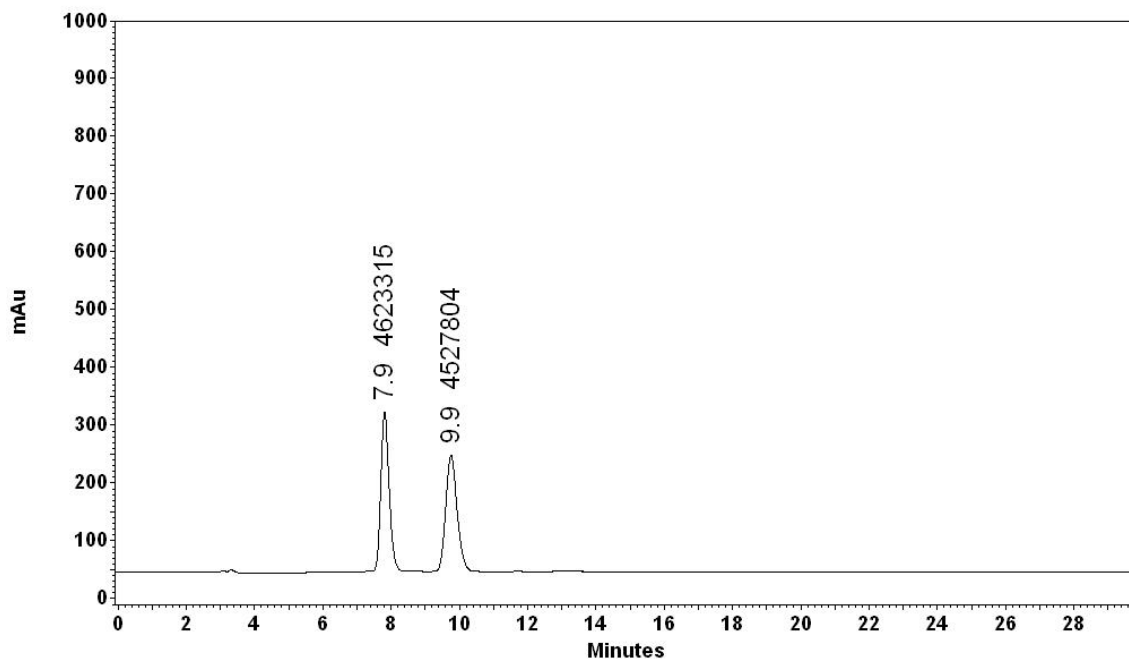
#### Reference HPLC Traces for Enantiomeric Assignment.

Reference HPLC traces were obtained with racemic ester derived from commercially obtained valinol and with independent samples of the esters derived from D- and L-valinol.

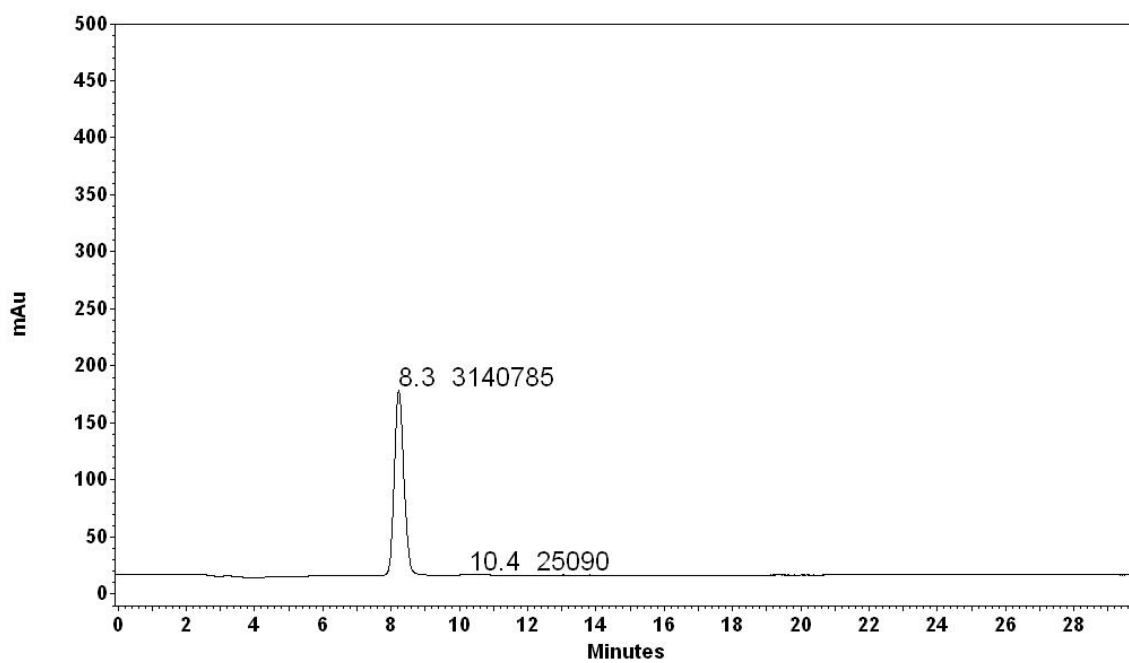
*Method for independent preparation of nitrobenzyl esters derived from Boc-DL-, Boc-D-, and Boc-L-valinol.*

NEt<sub>3</sub> (27  $\mu$ L, 0.2 mmol, 2 equiv) was added to a solution of the Boc-protected aminoalcohol (20 mg, 0.1 mmol, 1 equiv). The solution was cooled to 0  $^{\circ}$ C, then 4-nitrobenzoyl chloride (19 mg, 0.1 mmol, 1.05 equiv) was added. The resulting yellow solution was stirred for 16 h at room temperature, then diluted with 10% aq. CuSO<sub>4</sub> and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 30 mL). The organic layers were combined, washed with brine, dried over MgSO<sub>4</sub>, and concentrated in vacuo, yielding a yellow solid (37 mg, quant.) that was consistent with the desired product by <sup>1</sup>H NMR spectroscopy.

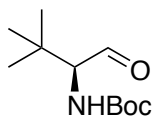
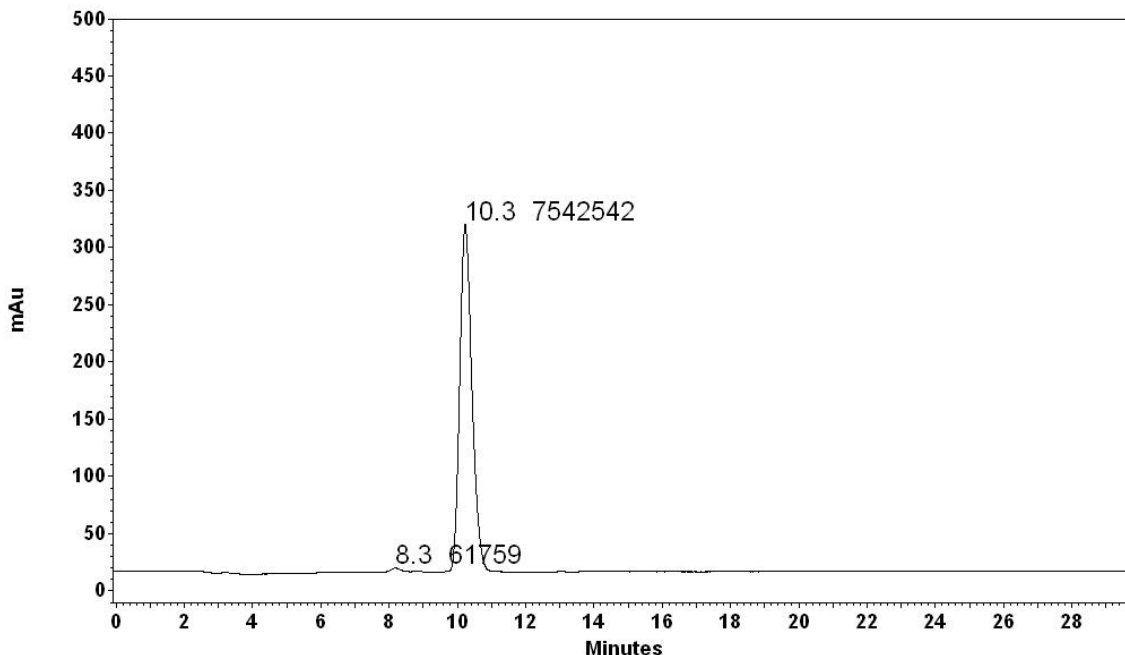
HPLC trace of racemic 2-((Boc)amino)-3-methylbutyl-4-nitrobenzoate. Chiralcel AS-*H*, 5-25% iPrOH, 1 mL/min, 254 nm



HPLC trace of (*S*)-2-((Boc)amino)-3-methylbutyl-4-nitrobenzoate. Chiralcel AS-*H*, 5-25% iPrOH, 1 mL/min, 254 nm



HPLC trace of (*R*)-2-((Boc)amino)-3-methylbutyl-4-nitrobenzoate. 98 % ee. Chiralcel AS-*H*, 5-25% iPrOH, 1 mL/min, 254 nm

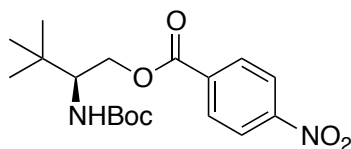


**19**

***N*-Boc-*L*-*tert*-leucinal.**

The reaction was run in a 25x150 mm test tube under air at room temperature for 1 h. The reaction mixture was purified according to *Method B* using Et<sub>2</sub>O as the organic layer, yielding the title compound as a light yellow solid (215 mg, >98 %). Isolated as a mixture of Boc rotamers. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.83 (s, 1H), 5.16 (d, *J* = 8.1 Hz, 1H), 4.18 (d, *J* = 8.6 Hz, 1H), 1.45 (s, 9H), 1.05 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 201.08, 155.93, 79.87, 67.43, 35.58, 28.29, 26.77. >99 % ee by HPLC analysis. Analysis of % ee shown in HPLC traces of (*R*)-2-((Boc)amino)-3,3-dimethylbutyl-4-nitrobenzoate below. Spectral properties are consistent with literature values.<sup>13</sup>

Note: Attempting to employ *Method A* or perform silica column chromatography to isolate this α-aminoaldehyde will result in epimerization of the stereocenter.



**(*R*)-2-((Boc)amino)-3,3-dimethylbutyl-4-nitrobenzoate.**

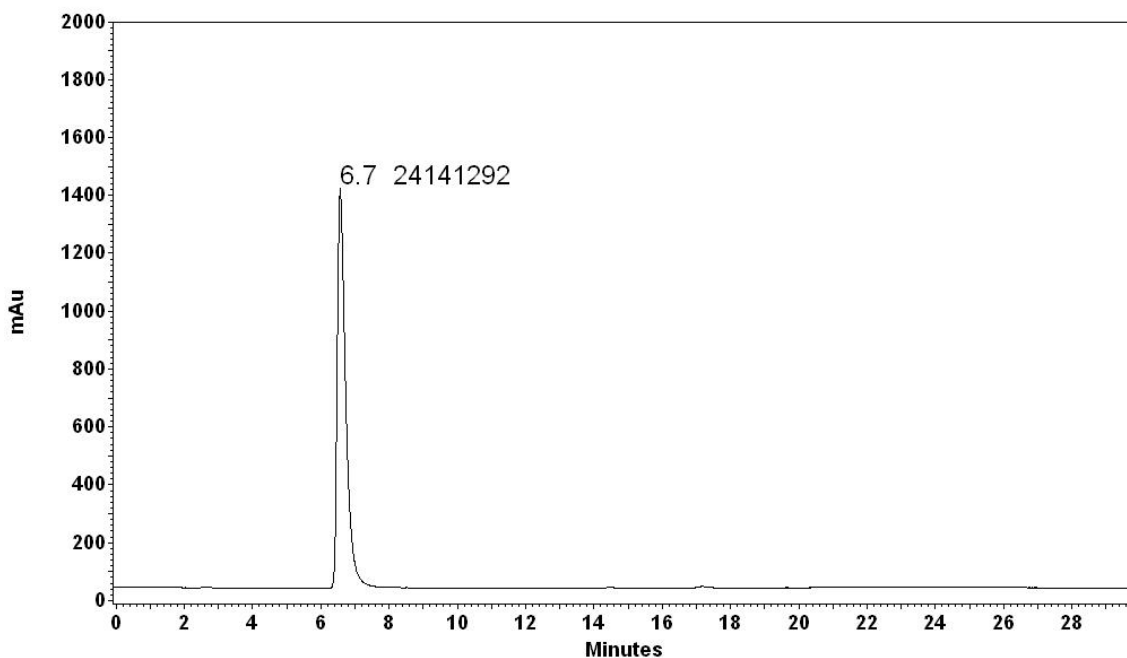
*N*-Boc-*L*-*tert*-leucinal (55 mg, 0.26 mmol, 1 equiv) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) and treated with NaBH<sub>4</sub> (150 mg, 3.96 mmol, 15.2 equiv). Upon completion of the reduction by TLC, the reaction mixture was quenched with the dropwise addition of sat. aq. NH<sub>4</sub>Cl and extracted with EtOAc (3 x 30 mL). The organic layers were combined, dried over



MgSO<sub>4</sub>, filtered, and concentrated in vacuo, yielding a yellow solid that was then redissolved in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) under N<sub>2</sub>. NEt<sub>3</sub> (72 μL, 0.52 mmol, 2 equiv) was added, followed by 4-nitrobenzoyl chloride (58 mg, 0.31 mmol, 1.2 equiv). The resulting yellow solution was stirred for 16 h at room temperature, then quenched with sat. aq. NH<sub>4</sub>Cl and extracted with EtOAc (3 x 30 mL). The organic layers were combined, washed with brine, dried over MgSO<sub>4</sub>, and concentrated in vacuo, yielding a yellow solid that was purified by silica column chromatography (10-20% EtOAc/hexanes gradient elution). The product was isolated as a clear oil (68 mg, 71 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.33 – 8.14 (m, 4H), 4.52 (dd, *J* = 11.3, 3.7 Hz, 2H), 4.29 (dd, *J* = 12, 12 Hz, 1H), 3.90 (td, *J* = 10.0, 3.6 Hz, 1H), 1.37 (s, 9H), 1.02 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.88, 155.97, 150.61, 135.47, 130.90, 123.48, 79.45, 65.71, 57.52, 33.58, 28.31, 26.68. HRMS (ESI) [*M*+H]<sup>+</sup>/*z* calcd. 367.1864, found 367.1862.

(*R*)-2-((Boc)amino)-3,3-dimethylbutyl-4-nitrobenzoate from 1 mmol scale oxidation of *N*-Boc-*L*-*tert*-leucinol.

Chiralcel OJ-*H*, 5-25% iPrOH, 1 mL/min, 254 nm, >99 % ee



#### Reference HPLC Traces for Enantiomeric Assignment.

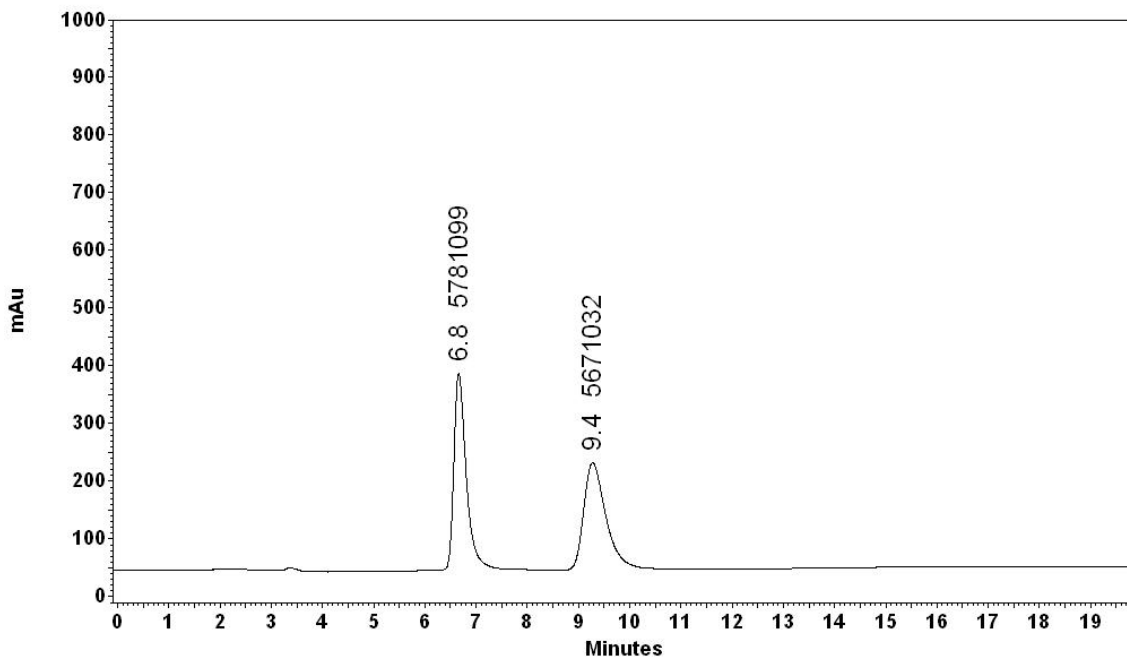
Reference HPLC traces were obtained with racemic ester derived from commercially obtained *tert*-leucinol and with independent samples of the esters derived from D- and L-*tert*-leucinol.

*Method for independent preparation of nitrobenzyl esters derived from Boc-DL-, Boc-D-, and Boc-L-tert-leucinol.*

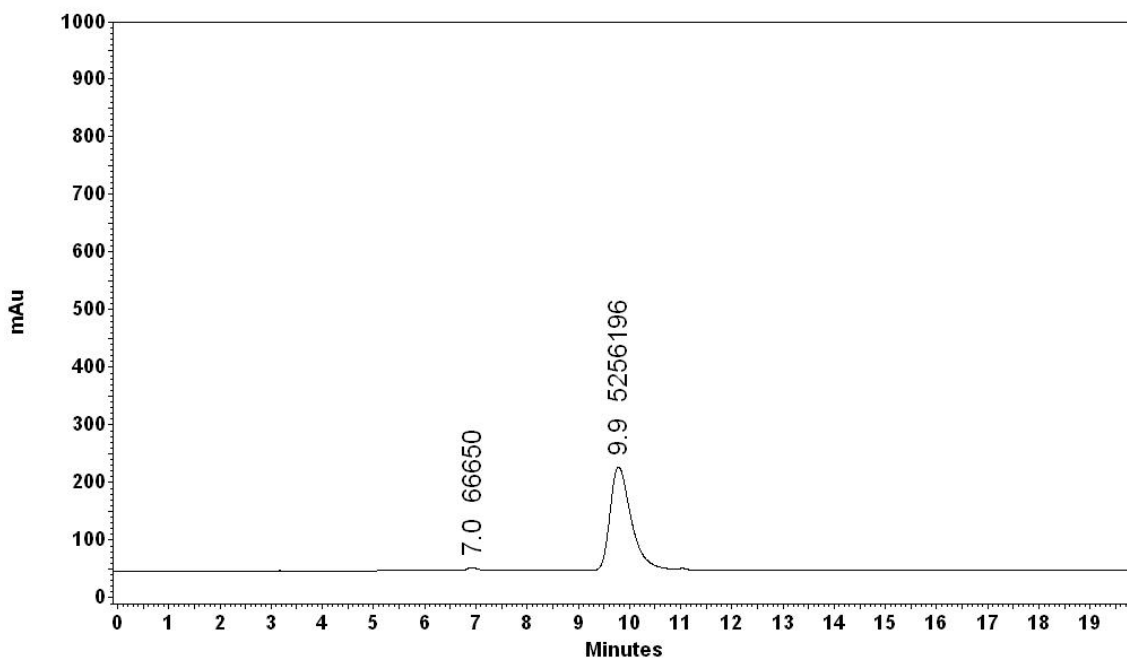
NEt<sub>3</sub> (26 μL, 0.18 mmol, 2 equiv) was added to a solution of the Boc-protected aminoalcohol (20 mg, 0.09 mmol, 1 equiv). The solution was cooled to 0 °C, then 4-nitrobenzoyl chloride (18 mg, 0.1 mmol, 1.05 equiv) was added. The resulting yellow solution was stirred for 16 h at room temperature, then diluted with 10% aq. CuSO<sub>4</sub> and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 30 mL). The organic layers were combined, washed with

brine, dried over  $\text{MgSO}_4$ , and concentrated in vacuo, yielding a yellow solid (33 mg, 98 %) that was consistent with the desired product by  $^1\text{H}$  NMR spectroscopy.

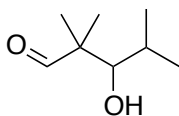
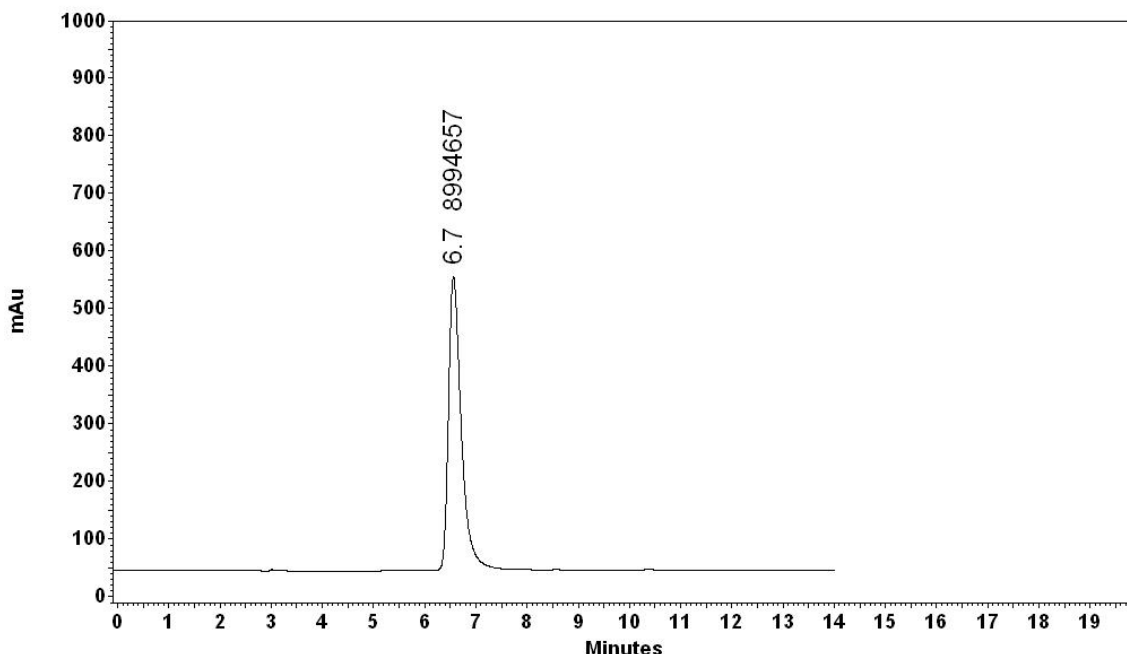
HPLC trace of racemic 2-((Boc)amino)-3,3-dimethylbutyl-4-nitrobenzoate. Chiralcel OJ-*H*, 5-25% iPrOH, 1 mL/min, 254 nm.



HPLC trace of (*S*)-2-((Boc)amino)-3,3-dimethylbutyl-4-nitrobenzoate. Chiralcel OJ-*H*, 5-25% iPrOH, 1 mL/min, 254 nm



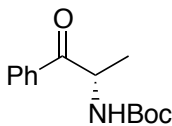
HPLC trace of (*R*)-2-((Boc)amino)-3,3-dimethylbutyl-4-nitrobenzoate. >99 % ee.  
Chiralcel OJ-*H*, 5-25% iPrOH, 1 mL/min, 254 nm



**20**

**2,2,4-trimethyl-3-hydroxy-1-pentanal.**

The reaction was run in a 25x150 mm test tube under an O<sub>2</sub> balloon at room temperature for 0.5 h. The reaction mixture was purified according to *Method B* using Et<sub>2</sub>O as the organic layer, yielding the title compound as a clear oil (144 mg, >98 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.63 (s, 1H), 3.55 (s, 1H), 2.05 (s, 1H), 1.88 (heptd, *J* = 6.8, 3.9 Hz, 1H), 1.13 (s, 3H), 1.12 (s, 3H), 0.97 (d, *J* = 6.9 Hz, 3H), 0.90 (d, *J* = 6.7 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 206.85, 80.29, 50.54, 29.93, 21.74, 19.86, 18.62, 17.22. Spectral properties are consistent with literature values.<sup>10</sup>



**21**

**(*S*)-*N*-Boc-cathinone.**

The reaction was run in a 25x150 mm test tube under air at room temperature for 0.75 h. The reaction mixture was purified according to *Method B* using Et<sub>2</sub>O as the organic layer, yielding the title compound as a white solid (236 mg, 95 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98 (d, *J* = 7.1 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 5.57 (d, *J* = 6.9 Hz, 1H), 5.33 – 5.26 (m, 1H), 1.46 (s, 9H), 1.40 (d, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 199.48, 155.19, 134.22, 133.73, 128.84, 128.68, 79.72, 51.11,

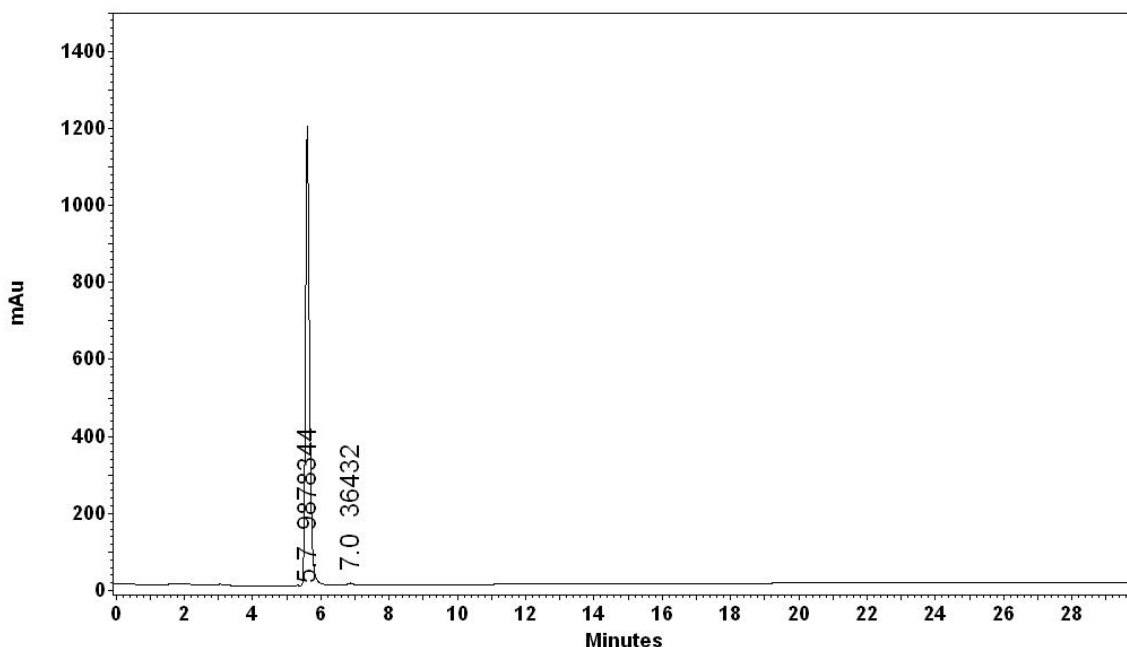
28.40, 19.94. >99 % ee based on HPLC analysis (see below). Spectral properties are consistent with literature values.<sup>2</sup>

Reaction (1 mmol) using 1 mol% Cu(MeCN)<sub>4</sub>OTf, 1 mol% <sup>MeO</sup>bpy, 1 mol% ABNO, 2 mol% NMI:

The reaction was performed in a 25x150 mm test tube under air at room temperature for 20 h. The reaction mixture was purified according to *Method B* using Et<sub>2</sub>O as the organic layer, yielding a yellow solid (213 mg, 86 %) that was confirmed to be pure desired product by <sup>1</sup>H NMR spectroscopy.

HPLC analysis of (*S*)-*N*-Boc-cathinone from 1 mmol oxidation of (*S*)-*N*-Boc-norephedrine.

Chiralcel OJ-*H*, 5-25% iPrOH, 1 mL/min, 254 nm, >99 % ee



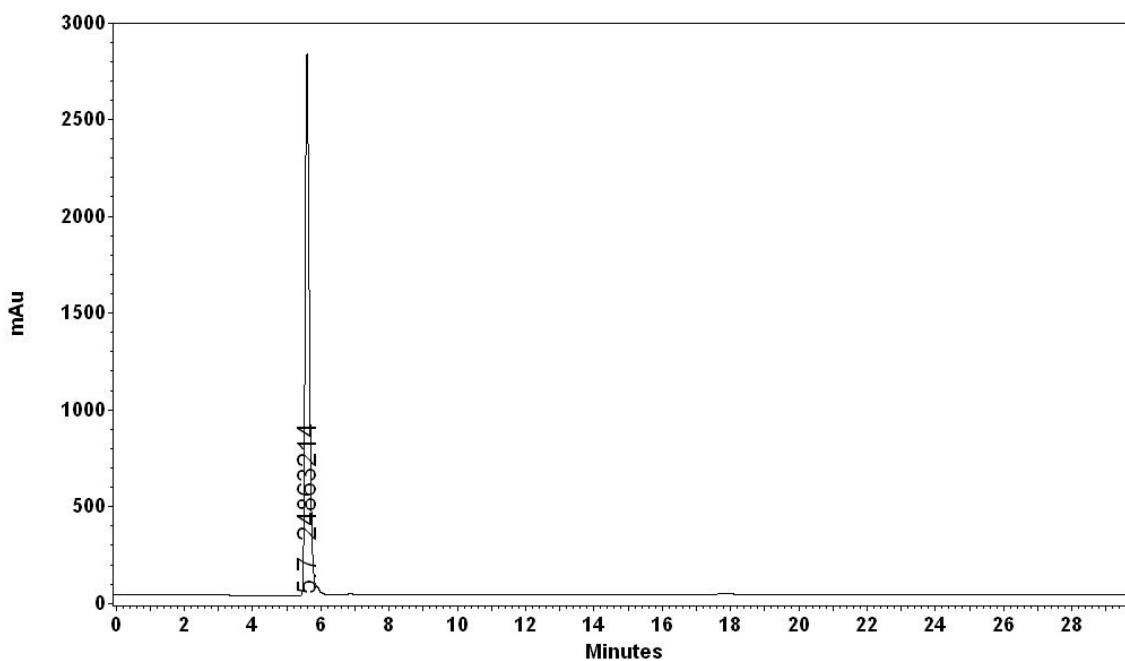
#### Reference HPLC Traces for Enantiomeric Assignment.

Reference HPLC traces were obtained racemic *N*-Boc-cathinone and with an independent sample of (*S*)-*N*-Boc-cathinone prepared via the method described below.

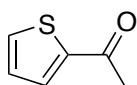
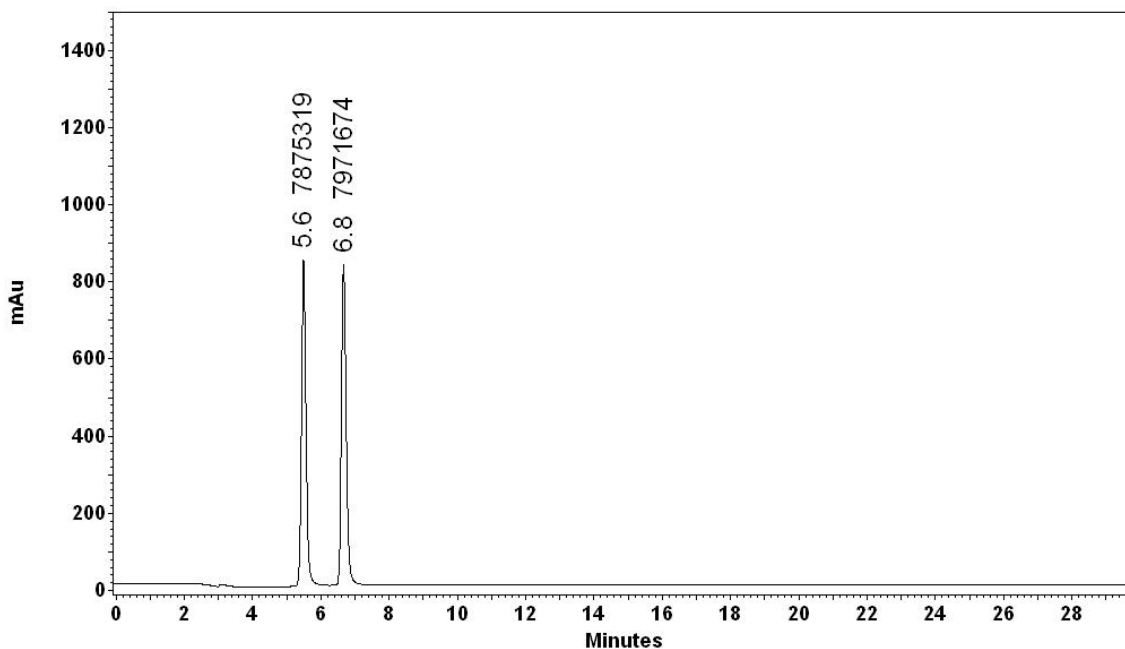
#### *Method for independent preparation of (S)-N-Boc-cathinone.*<sup>14</sup>

Dess Martin periodinane (445 mg, 1.05 mmol, 2.1 equiv) was added in one portion to a stirred solution of Boc-LD-norephedrine (126 mg, 0.5 mmol, 1 equiv) in H<sub>2</sub>O-saturated CH<sub>2</sub>Cl<sub>2</sub> (2 mL) at room temperature. The reaction was stirred for 20 min, then diluted with Et<sub>2</sub>O (10 mL), sat. aq. NaHCO<sub>3</sub> (8 mL), and H<sub>2</sub>O (2 mL). The reaction was stirred until both layers were clear, then diluted with sat. aq. NaHCO<sub>3</sub> and extracted with Et<sub>2</sub>O (3 x 30 mL). The organic layers were combined, washed with H<sub>2</sub>O (2x), brine, and dried over MgSO<sub>4</sub>. The filtrate was concentrated in vacuo, yielding a white solid (121 mg, 97 %) that was consistent with the desired product by <sup>1</sup>H NMR spectroscopy.

Chiralcel OJ-*H*, 5-25% iPrOH, 1 mL/min, 254 nm: analysis of (*S*)-*N*-Boc-cathinone.



Chiralcel OJ-*H*, 5-25% iPrOH, 1 mL/min, 254 nm: analysis of racemic *N*-Boc-cathinone.

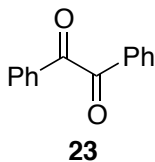


**22**

**2-acetyl-thiophene.**

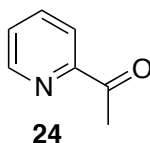
The reaction was run in a 25x150 mm test tube under air at room temperature for 1 h. The reaction mixture was purified according to *Method B* using Et<sub>2</sub>O as the organic layer,

yielding the title compound as a yellow oil (120 mg, 95 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (dd,  $J$  = 3.8, 1.1 Hz, 1H), 7.64 (dd,  $J$  = 5.0, 1.1 Hz, 1H), 7.13 (dd,  $J$  = 5.0, 3.8 Hz, 1H), 2.57 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  190.78, 144.59, 133.82, 132.50, 128.13, 26.96. Spectral properties are consistent with literature values.<sup>15</sup>



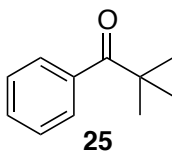
#### benzil.

Benzoin was used as the starting material. The reaction was run in a 25x150 mm test tube under air at room temperature for 1 h. The reaction mixture was purified according to *Method A*, yielding the title compound as a light yellow solid (206 mg, 98 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J$  = 7.0 Hz, 4H), 7.66 (t,  $J$  = 7.4 Hz, 2H), 7.52 (t,  $J$  = 7.8 Hz, 4H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  194.60, 134.92, 133.00, 129.94, 129.05. Spectral properties are consistent with literature values.<sup>10</sup>



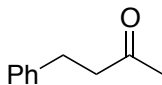
#### 2-acetyl-pyridine.

The reaction was run in a 25x150 mm test tube under an  $\text{O}_2$  balloon at 70 °C for 1.5 h. At this point, a solution of  $\text{Cu}(\text{MeCN})_4\text{OTf}$  (7.5 mg, 0.02 mmol, 0.02 equiv),  $^{\text{MeO}}\text{bpy}$  (4.3 mg, 0.02 mmol, 0.02 equiv), ABNO (1.4 mg, 0.01 mmol, 0.01 equiv), and NMI (3.2  $\mu\text{L}$ , 0.04 mmol, 0.04 equiv) in MeCN (500  $\mu\text{L}$ ) was added and the reaction was stirred under  $\text{O}_2$  at 70 °C for an additional 0.5 h. The reaction mixture was purified according to *Method B* using  $\text{Et}_2\text{O}$  as the organic layer and sat. aq.  $\text{NaHCO}_3$  as the aqueous layer, yielding the title compound as a brown oil (93 mg, 77 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.69 (d,  $J$  = 4.5 Hz, 1H), 8.05 (dt,  $J$  = 7.9, 1.1 Hz, 1H), 7.84 (td,  $J$  = 7.7, 1.8 Hz, 1H), 7.47 (ddd,  $J$  = 7.6, 4.8, 1.3 Hz, 1H), 2.73 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  200.28, 153.76, 149.15, 137.00, 127.25, 121.81, 25.96. Spectral properties are consistent with literature values.<sup>10</sup>



#### 2,2-dimethyl-1-phenyl-1-propanone.

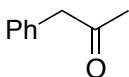
The reaction was run in a 25x150 mm test tube under air at room temperature for 1 h. The reaction mixture was purified according to *Method A*, yielding the title compound as a light yellow oil (147 mg, 91 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (d,  $J$  = 6.9 Hz, 2H), 7.45 (t,  $J$  = 7.3 Hz, 1H), 7.39 (t,  $J$  = 7.3 Hz, 2H), 1.35 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  209.29, 138.62, 130.82, 128.06, 127.84, 44.22, 28.04. Spectral properties are consistent with literature values.<sup>10</sup>



26

**4-phenyl-2-butanone.**

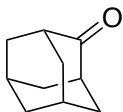
The reaction was run in a 25x150 mm test tube under air at room temperature for 1 h. The reaction mixture was purified according to *Method B*, yielding the title compound as a clear oil (140 mg, 95 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 – 7.26 (m, 2H), 7.20 – 7.17 (m, 3H), 2.89 (t,  $J = 7.6$  Hz, 2H), 2.76 (t,  $J = 7.6$  Hz, 2H), 2.13 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  207.94, 141.01, 128.52, 128.31, 126.14, 45.20, 30.09, 29.77. Spectral properties are consistent with literature values.<sup>10</sup>



27

**1-phenyl-2-propanone.**

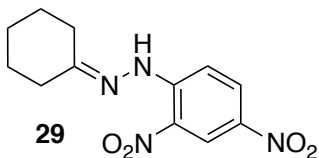
The reaction was run in a 25x150 mm test tube under air at room temperature for 1 h. The reaction mixture was purified according to *Method B*, yielding the title compound as a light yellow oil (127 mg, 95 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 (t,  $J = 7.3$  Hz, 2H), 7.27 (t,  $J = 8$  Hz, 1H), 7.20 (d,  $J = 6.7$  Hz, 2H), 3.69 (s, 2H), 2.15 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  206.41, 134.27, 129.41, 128.78, 127.09, 51.06, 29.28. Spectral properties are consistent with literature values.<sup>16</sup>



28

**2-adamantanone.**

The reaction was run in a 25x150 mm test tube under air at room temperature for 1 h. The reaction mixture was purified according to *Method A*, yielding the title compound as a white solid (147 mg, 98 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.55 (s, 2H), 2.15 – 1.91 (m, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  218.53, 46.99, 39.28, 36.32, 27.47. Spectral properties are consistent with commercially available product.

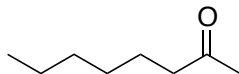


29

**cyclohexanone-(2,4-dinitrophenylhydrazone).**

The reaction was run in a 25x150 mm test tube under air at room temperature for 1 h. Upon completion by TLC, the blue solution was treated with  $\text{H}_2\text{O}$  (4 mL),  $\text{HCl}$  (500  $\mu\text{L}$ , 6M aq.), then 2,4-dinitrophenylhydrazine (204 mg, 1.03 mmol, 1.03 equiv). Formation of the hydrazone was indicated by appearance of a bright yellow precipitate. After 1 h, the reaction was complete by TLC. The slurry was diluted with  $\text{H}_2\text{O}$  (40 mL) and extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 40 mL). The organic layers were combined, dried over

MgSO<sub>4</sub>, and concentrated in vacuo. The resulting yellow solid was re-dissolved in CH<sub>2</sub>Cl<sub>2</sub>, filtered through a plug of silica (1 cm) to remove excess hydrazine, and rinsed with CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was concentrated in vacuo, affording the title compound as a yellow crystalline solid (267 mg, 96 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 11.20 (s, 1H), 9.12 (d, *J* = 2.6 Hz, 1H), 8.28 (dd, *J* = 9.7, 2.6 Hz, 1H), 7.97 (d, *J* = 9.7 Hz, 1H), 2.50 – 2.45 (m, 4H), 1.92 – 1.67 (m, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.44, 145.35, 137.48, 129.94, 128.83, 123.62, 116.25, 35.60, 27.23, 27.05, 26.01, 25.50. HRMS (ESI) [M+H]<sup>+</sup>/*z* calcd. 279.1088, 279.1080.



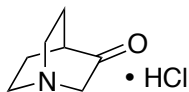
**30**

### 2-octanone.

The reaction was run in a 25x150 mm test tube under air at room temperature for 1 h. The reaction mixture was purified according to *Method B*, yielding the title compound as a clear oil (123 mg, 96 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.42 (t, *J* = 7.5 Hz, 2H), 2.13 (s, 3H), 1.60 – 1.53 (m, 2H), 1.33 – 1.26 (m, 6H), 0.90 – 0.86 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 209.42, 43.84, 31.61, 29.86, 28.87, 23.85, 22.51, 14.04. Spectral properties are consistent with commercially available product.

10 mmol scale reaction:

The reaction was run in a 500 mL round-bottom flask open to air with 1 x 0.5-inch oval stirbar. After 1 h, the reaction was complete by TLC and diluted with 200 mL H<sub>2</sub>O. The aqueous layer was extracted with pentanes (3 x 200 mL). The organic layers were combined, washed with brine, and dried over MgSO<sub>4</sub>, then concentrated in vacuo. A slightly colored oil (1.24 g, 96%) was isolated and consistent with the desired product by <sup>1</sup>H NMR spectroscopy.

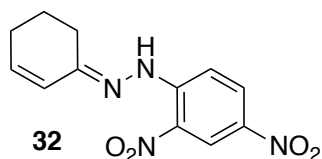


**31**

### 3-quinuclidone hydrochloride.

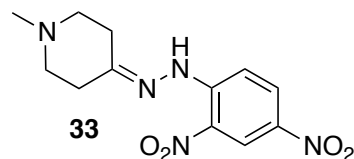
The reaction was run in a 25x150 mm test tube under an O<sub>2</sub> balloon at 70 °C for 1.5 h. At this point, blue solution cooled to room temperature and treated 35 drops of aq. NH<sub>4</sub>OH (28.0 – 30.0 % NH<sub>3</sub> basis) and dried over MgSO<sub>4</sub>. When the solution was clear and MgSO<sub>4</sub> was blue, the slurry was gravity filtered and the filtrate was treated with a solution of HCl in Et<sub>2</sub>O (1 mL, 2 mmol, 2 equiv). A yellow precipitate formed and the resulting slurry was stirred for 30 min, then filtered and washed with Et<sub>2</sub>O, affording the product as a yellow solid (132 mg, 82 %). <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O) δ 4.07 – 4.04 (m, 1H), 3.70 – 3.41 (m, 3H), 3.40 – 3.21 (m, 3H), 2.88 – 2.85 (m, 1H), 2.47 – 2.09 (m, 4H), 2.00 – 1.91 (m, 1H). Spectral properties are consistent with commercially available product.





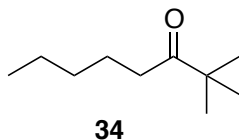
**2-cyclohexenone-(2,4-dinitrophenylhydrazone).**

The reaction was run in a 25x150 mm test tube under air at room temperature for 1 h. Upon completion by TLC, the blue solution was treated with H<sub>2</sub>O (4 mL), HCl (500  $\mu$ L, 6M aq.), then 2,4-dinitrophenylhydrazine (204 mg, 1.03 mmol, 1.03 equiv). Formation of the hydrazone was indicated by appearance of a bright red precipitate. After 1 h, the reaction was complete by TLC. The slurry was diluted with H<sub>2</sub>O (40 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 40 mL). The organic layers were combined, dried over MgSO<sub>4</sub>, and concentrated in vacuo. The resulting yellow solid was re-dissolved in CH<sub>2</sub>Cl<sub>2</sub>, filtered through a plug of silica (1 cm) to remove excess hydrazine, and rinsed with CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was concentrated in vacuo, affording the title compound as a red solid (277 mg, >98 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  11.25 (s, 1H), 9.13 (d, *J* = 2.6 Hz, 1H), 8.31 (dd, *J* = 9.6, 2.6 Hz, 1H), 8.00 (d, *J* = 9.6 Hz, 1H), 6.46 (dt, *J* = 8, 4 Hz, 1H), 6.34 (dt, *J* = 10.1, 1.9 Hz, 1H), 2.61 (dd, *J* = 6.7, 6.7 Hz, 2H), 2.34 – 2.29 (m, 2H), 2.00 – 1.93 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  154.09, 144.79, 138.93, 137.91, 130.00, 129.97, 127.28, 123.54, 116.53, 24.91, 24.24, 21.02. HRMS (ESI) [M+H]<sup>+</sup>/*z* calcd. 277.0932, found 277.0935.



**1-methyl-piperidin-4-one-(2,4-dinitrophenylhydrazone).**

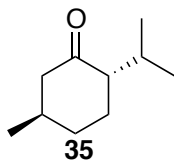
The reaction was run in a 25x150 mm test tube under air at room temperature for 1 h. Upon completion by TLC, the blue solution was treated with H<sub>2</sub>O (4 mL), HCl (500  $\mu$ L, 6M aq.), then 2,4-dinitrophenylhydrazine (204 mg, 1.03 mmol, 1.03 equiv). After 2 h, the slurry was diluted with sat. aq. NaHCO<sub>3</sub> (40 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 40 mL). The organic layers were combined, washed with sat. NaHCO<sub>3</sub>, dried over MgSO<sub>4</sub>, and concentrated in vacuo, affording the title compound as a brown crystalline solid (267 mg, 91 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  11.18 (s, 1H), 9.12 (d, *J* = 2.6 Hz, 1H), 8.30 (dd, *J* = 9.6, 2.6 Hz, 1H), 7.97 (d, *J* = 9.6 Hz, 1H), 2.63 (s, 4H), 2.62 (s, 4H), 2.39 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  157.29, 145.26, 137.76, 130.03, 129.03, 123.56, 116.27, 55.74, 54.25, 45.75, 34.75, 27.04. HRMS (ESI) [M+H]<sup>+</sup>/*z* calcd. 297.1197, found 297.1190.



**2,2-dimethyl-3-octanone.**

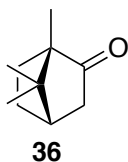
The reaction was run in a 25x150 mm test tube under an air balloon at 60 °C for 1 h. The reaction mixture was purified according to *Method B*, yielding the title compound as a

clear oil (154 mg, >98 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.47 (t,  $J = 7.3$  Hz, 2H), 1.59 – 1.52 (m, 2H), 1.43 – 1.19 (m, 4H), 1.13 (s, 9H), 0.89 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  216.14, 44.09, 36.41, 31.53, 26.41, 23.64, 22.56, 13.96. Spectral properties are consistent with literature values.<sup>17</sup>



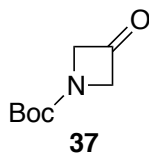
**(-)-menthone.**

The reaction was run in a 25x150 mm test tube under an  $\text{O}_2$  balloon at 70 °C for 1 h. The reaction mixture was purified according to *Method B*, yielding the title compound as a clear oil (138 mg, 89 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.36 (ddd,  $J = 16, 4, 4$  Hz, 1H), 2.24 – 1.76 (m, 6H), 1.49 – 1.24 (m, 2H), 1.01 (d,  $J = 6.3$  Hz, 3H), 0.92 (d,  $J = 6.8$  Hz, 3H), 0.86 (d,  $J = 6.8$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  212.36, 55.91, 50.89, 35.48, 33.95, 27.89, 25.92, 22.29, 21.22, 18.71. Spectral properties are consistent with literature values.<sup>10</sup>



**camphor.**

The reaction was run in a 25x150 mm test tube under an  $\text{O}_2$  balloon at 70 °C for 1 h. The reaction mixture was purified according to *Method A* using EtOAc as the eluent, yielding the title compound as a light yellow solid (117 mg, 77 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.42 – 2.25 (ddd,  $J = 20, 4, 4$  Hz, 1H), 2.09 (t,  $J = 4.5$  Hz, 1H), 1.95 (ddt,  $J = 16.3, 7.6, 3.9$  Hz, 1H), 1.84 (d,  $J = 18.2$  Hz, 1H), 1.68 (td,  $J = 12.0, 10.9, 3.4$  Hz, 1H), 1.49 – 1.26 (m, 2H), 0.96 (s, 3H), 0.91 (s, 3H), 0.84 (s, 3H). Spectral properties are consistent with commercially available product.



**1-Boc-3-azetidinone.**

The reaction was run in a 25x150 mm test tube under air at room temperature for 0.5 h. The reaction mixture was purified according to *Method B* using  $\text{Et}_2\text{O}$  as the organic layer, yielding the title compound as a yellow solid (167 mg, 98 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.69 (s, 4H), 1.49 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.62, 156.03, 80.98, 71.01, 28.25. Spectral properties are consistent with commercially available product.

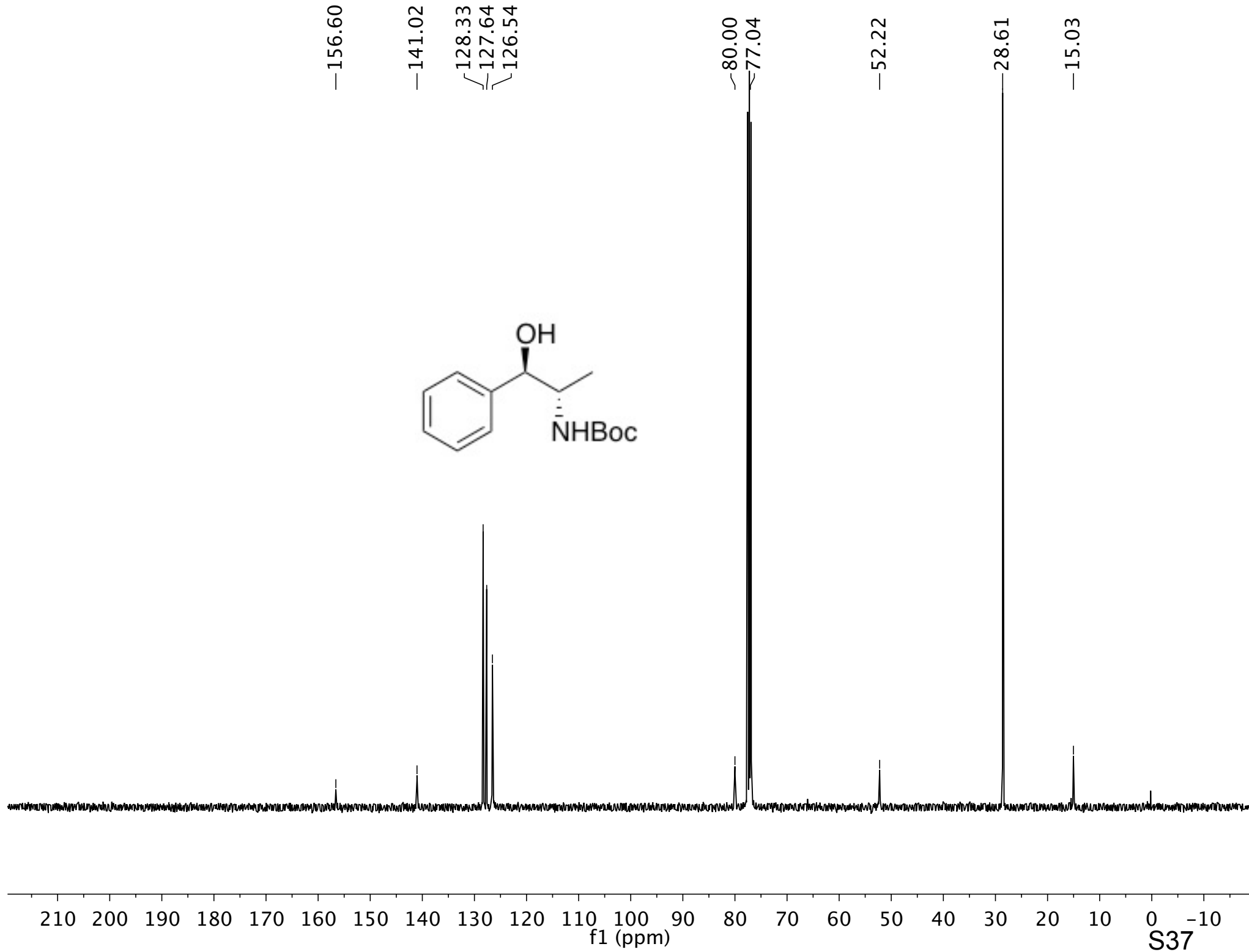
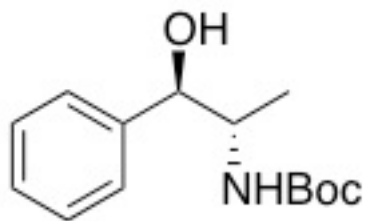
50 mmol scale reaction:

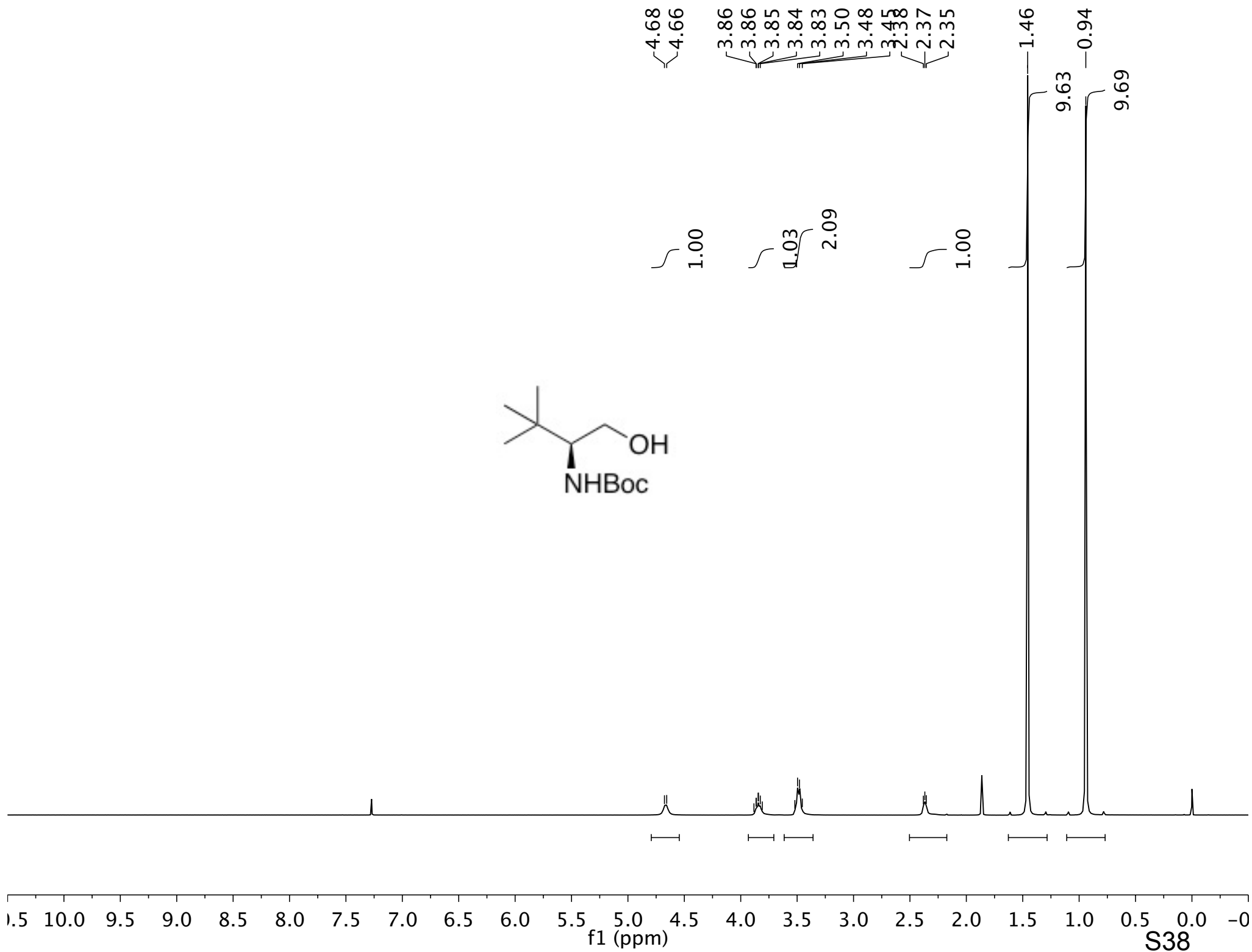
The reaction was run in a 1 L round-bottom flask with 250 mL MeCN open to air with 1 x 0.5-inch oval stirbar. After 3 h, the reaction was complete by TLC and diluted with 600 mL H<sub>2</sub>O. The aqueous layer was extracted with Et<sub>2</sub>O (3 x 600 mL). The organic layers were combined, washed with brine, and dried over MgSO<sub>4</sub>, then concentrated in vacuo. A white solid (7.58 g, 89 %) was isolated and consistent with the desired product by <sup>1</sup>H NMR spectroscopy.

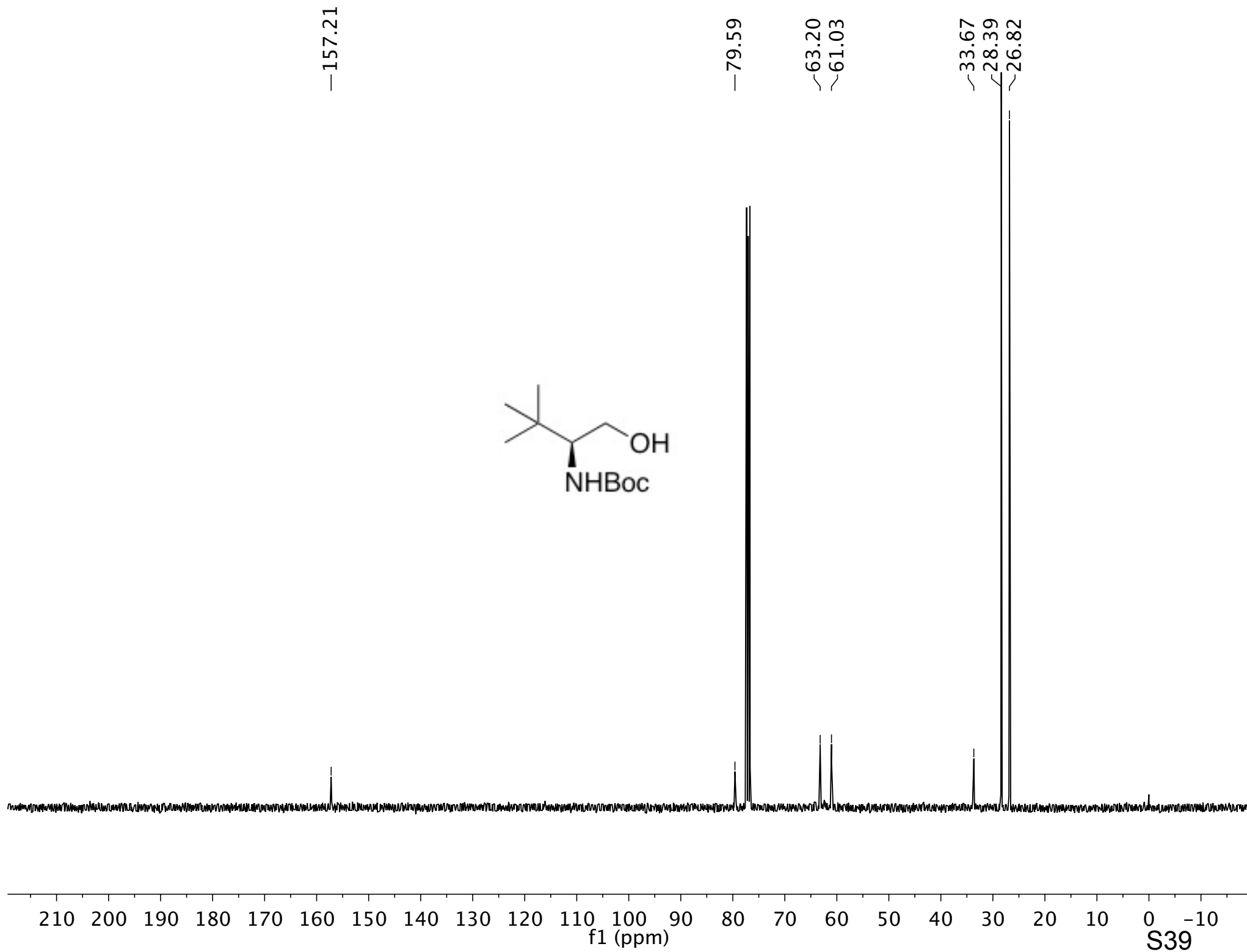
## References

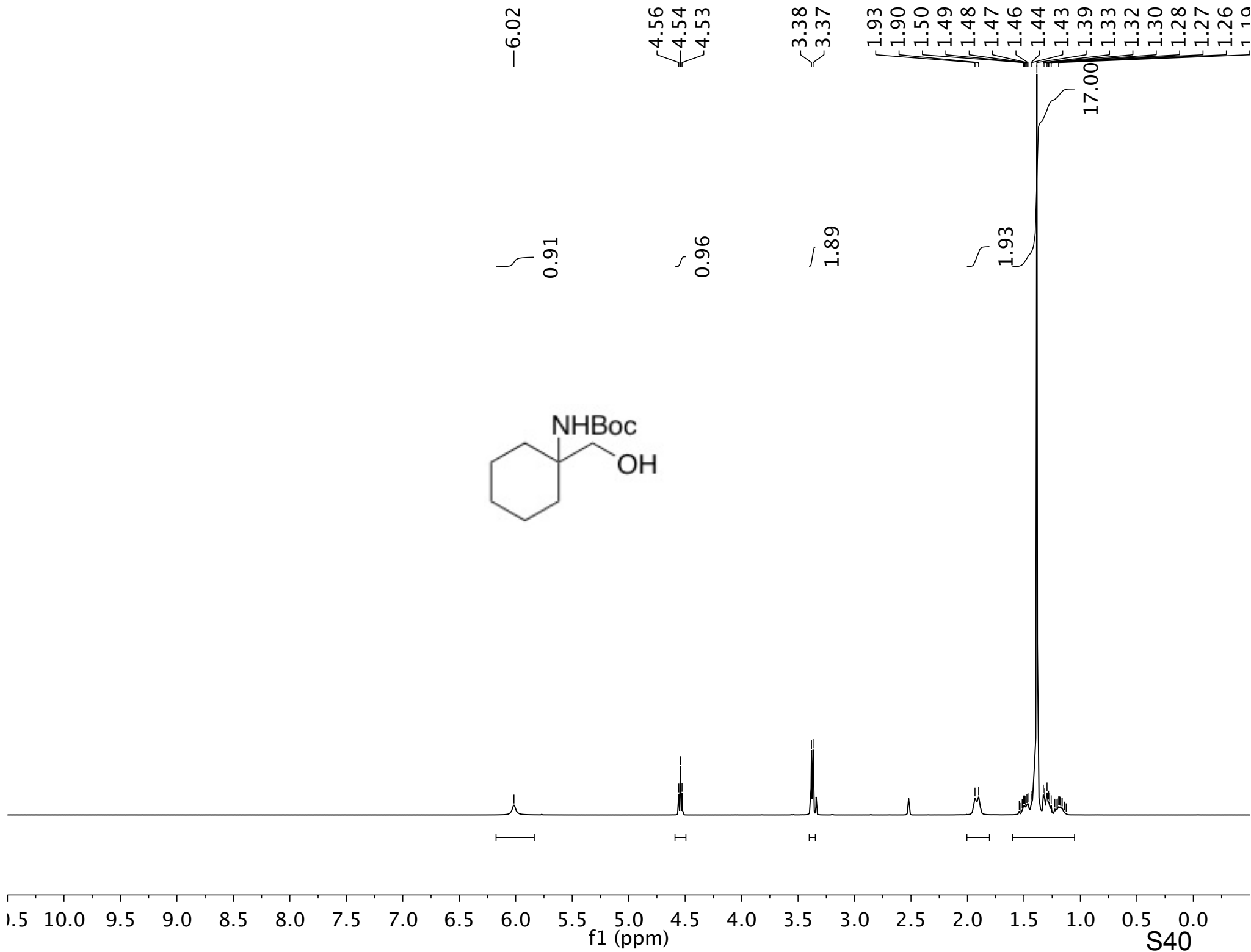
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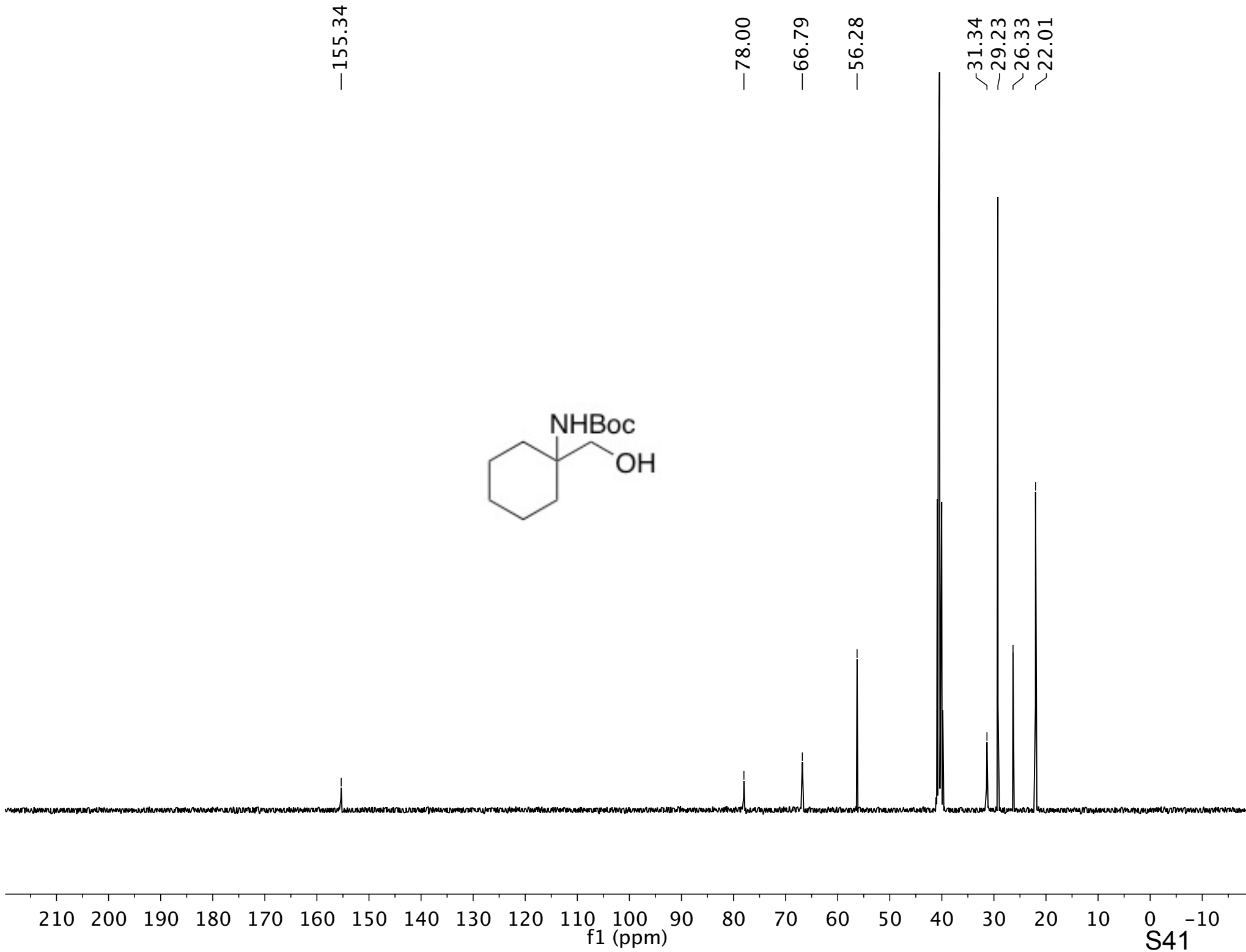
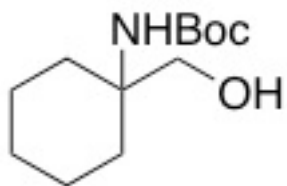


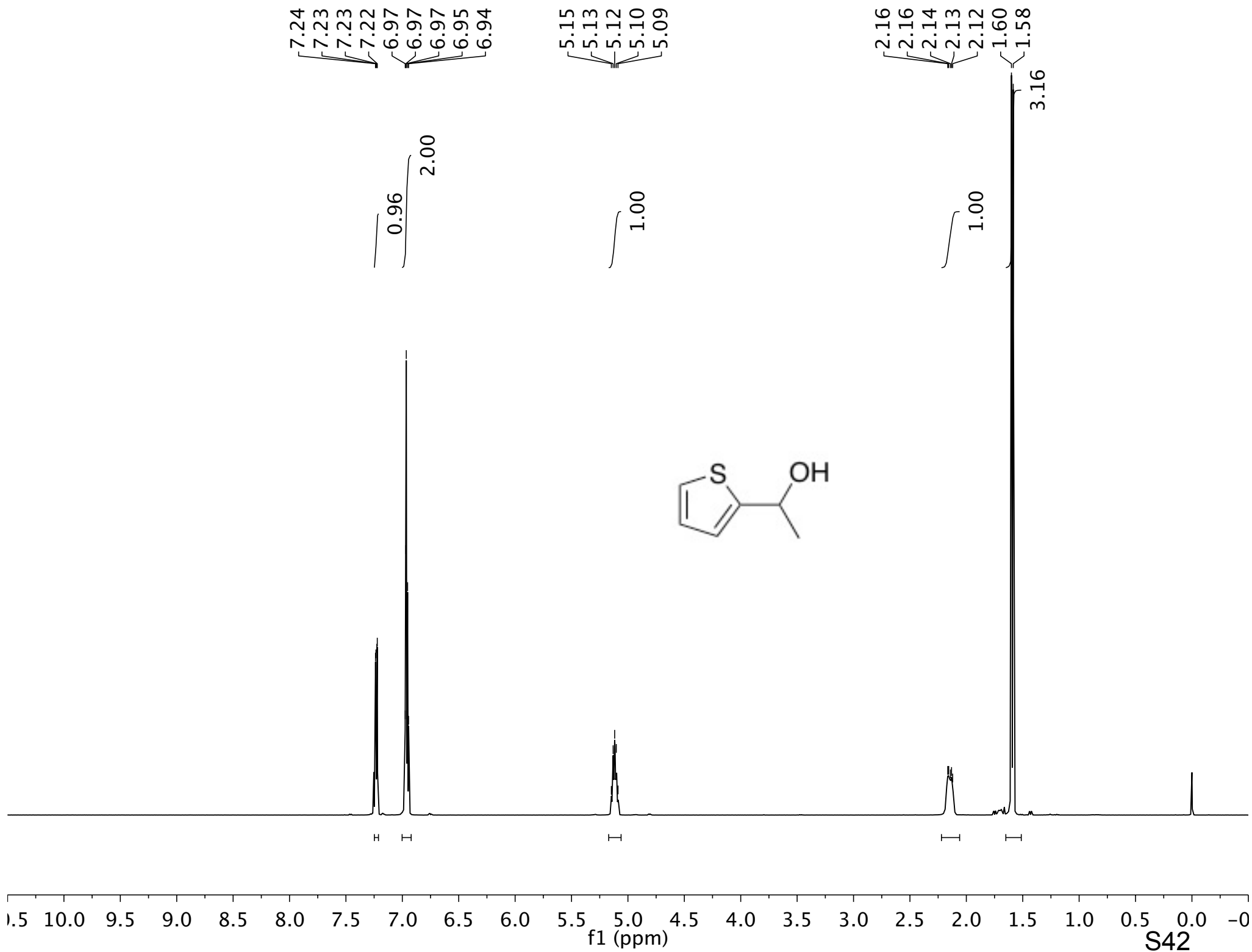


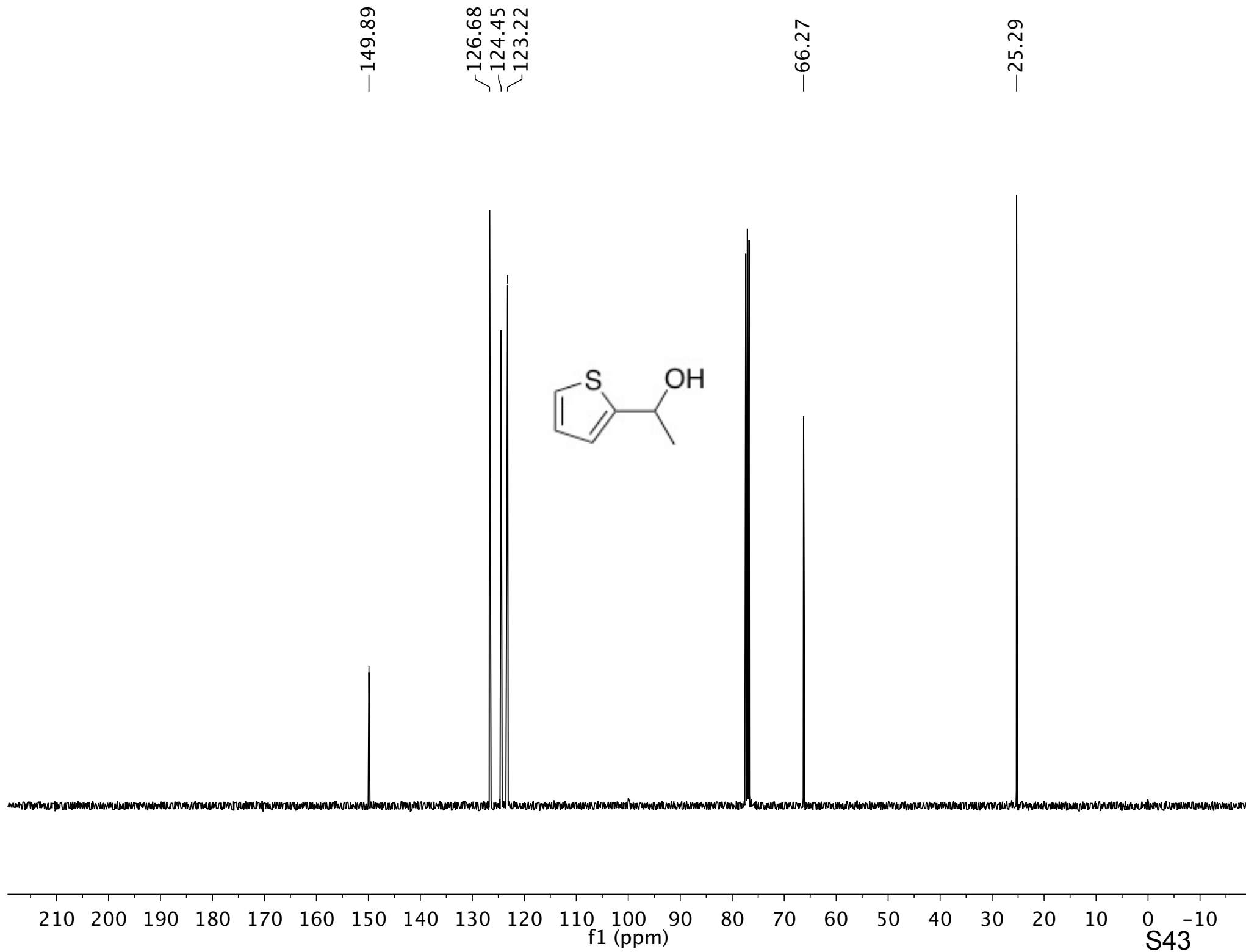


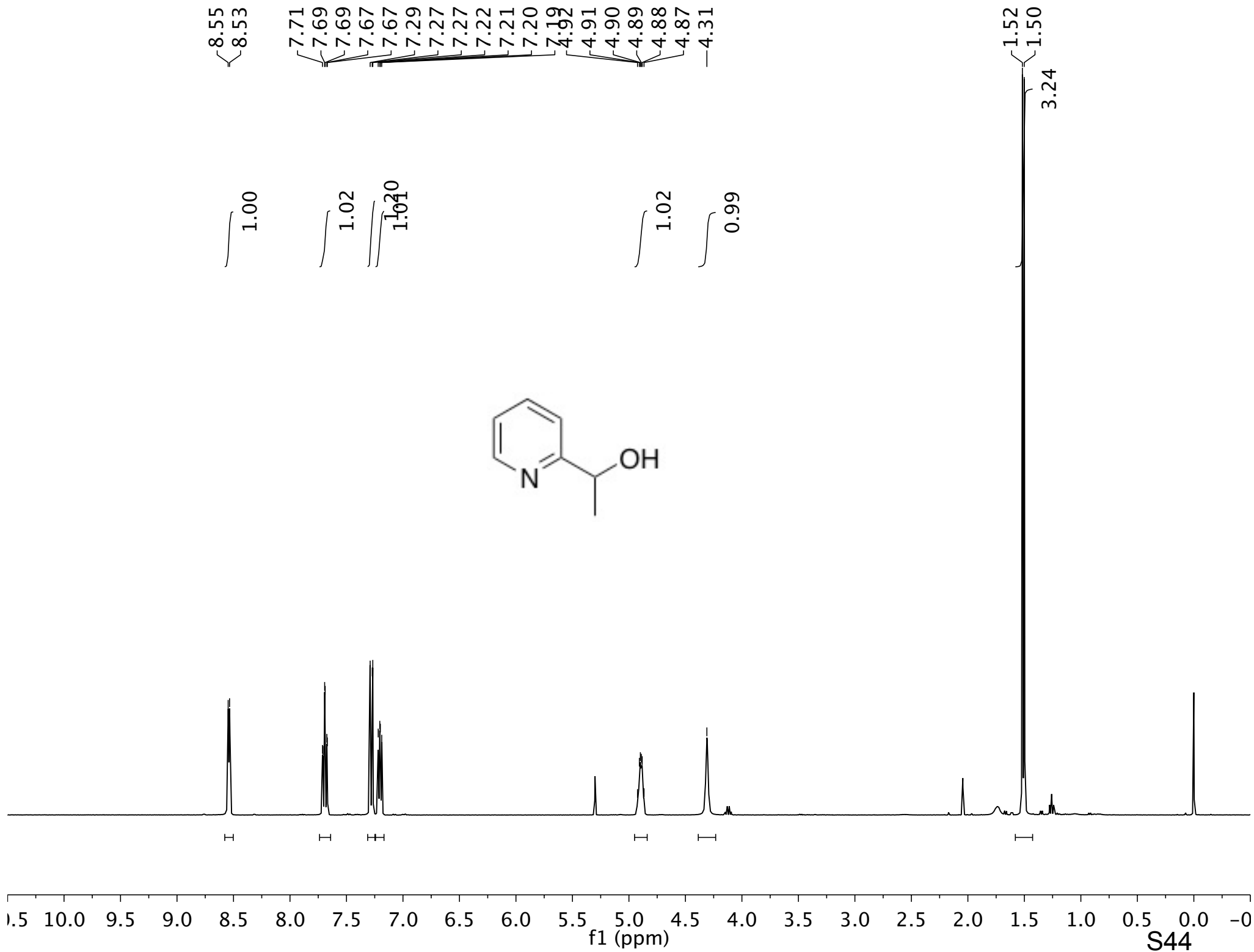


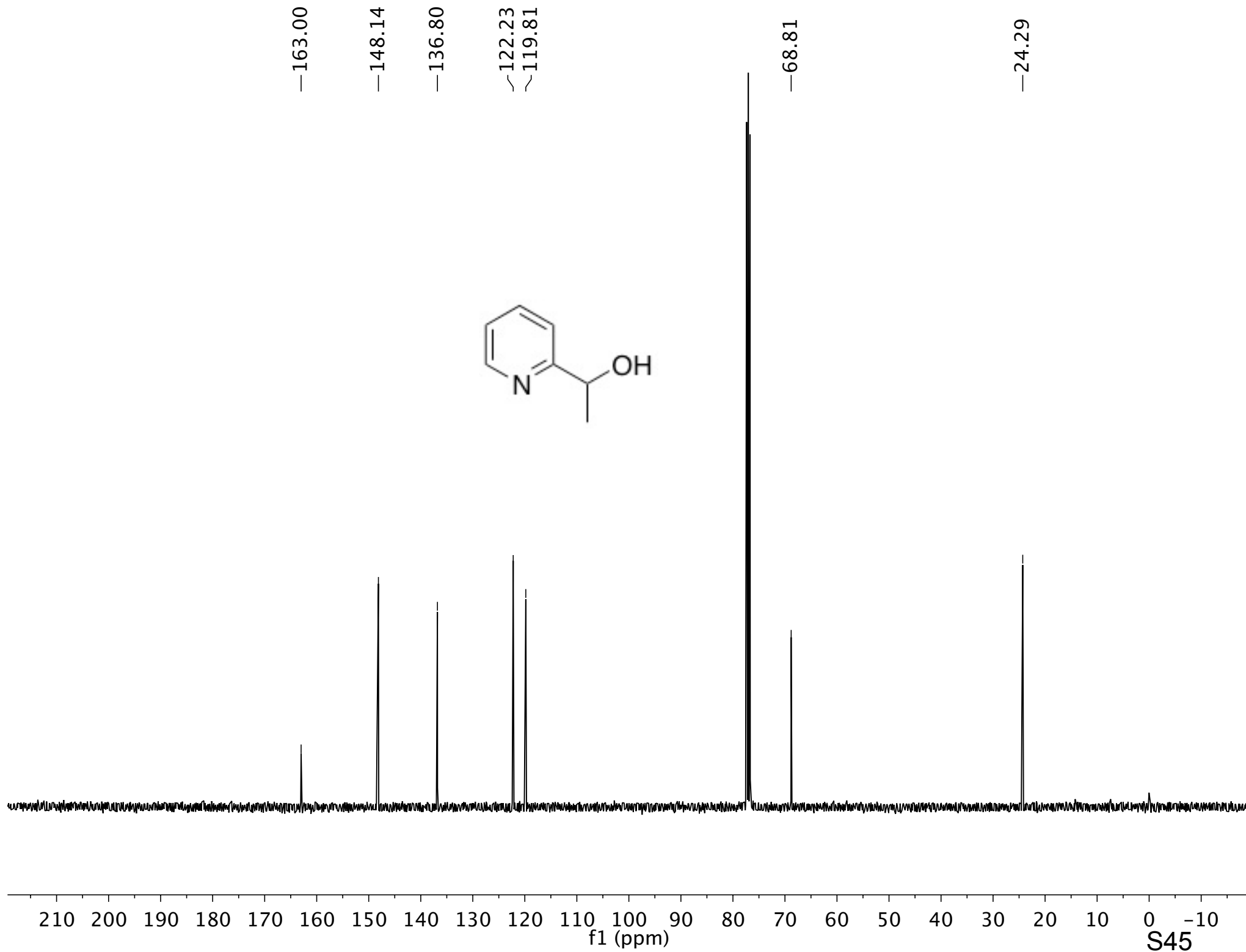
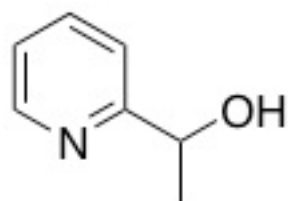


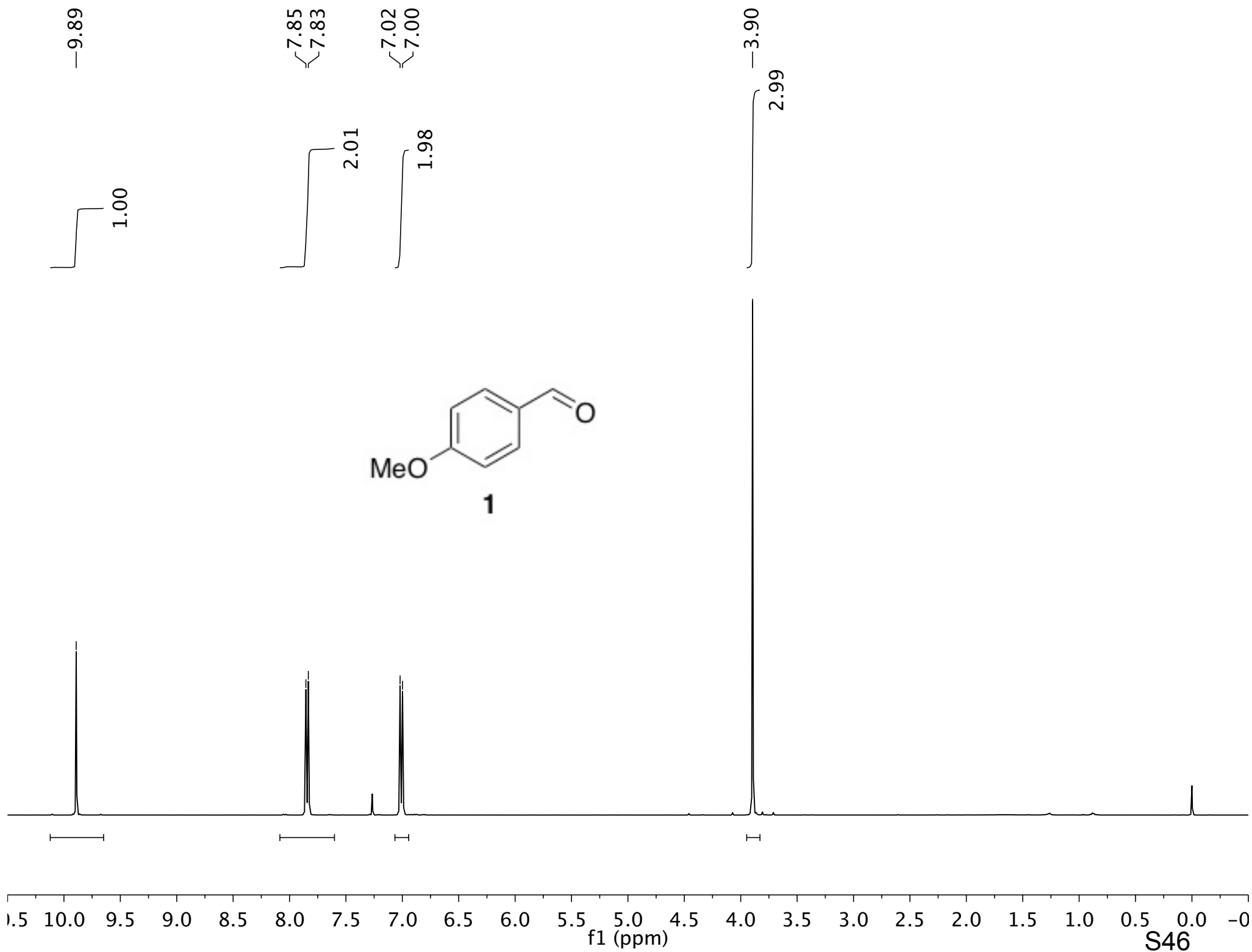


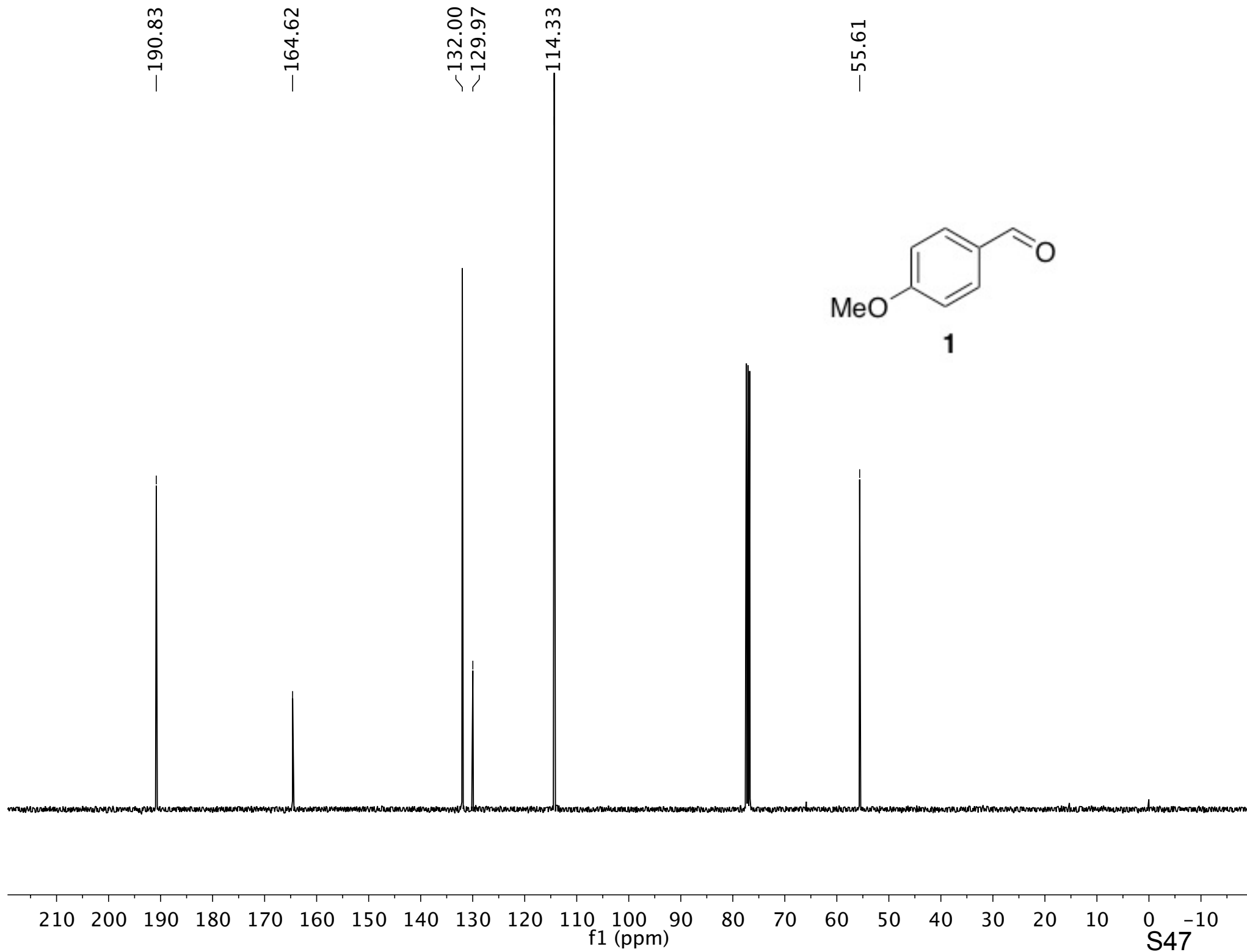






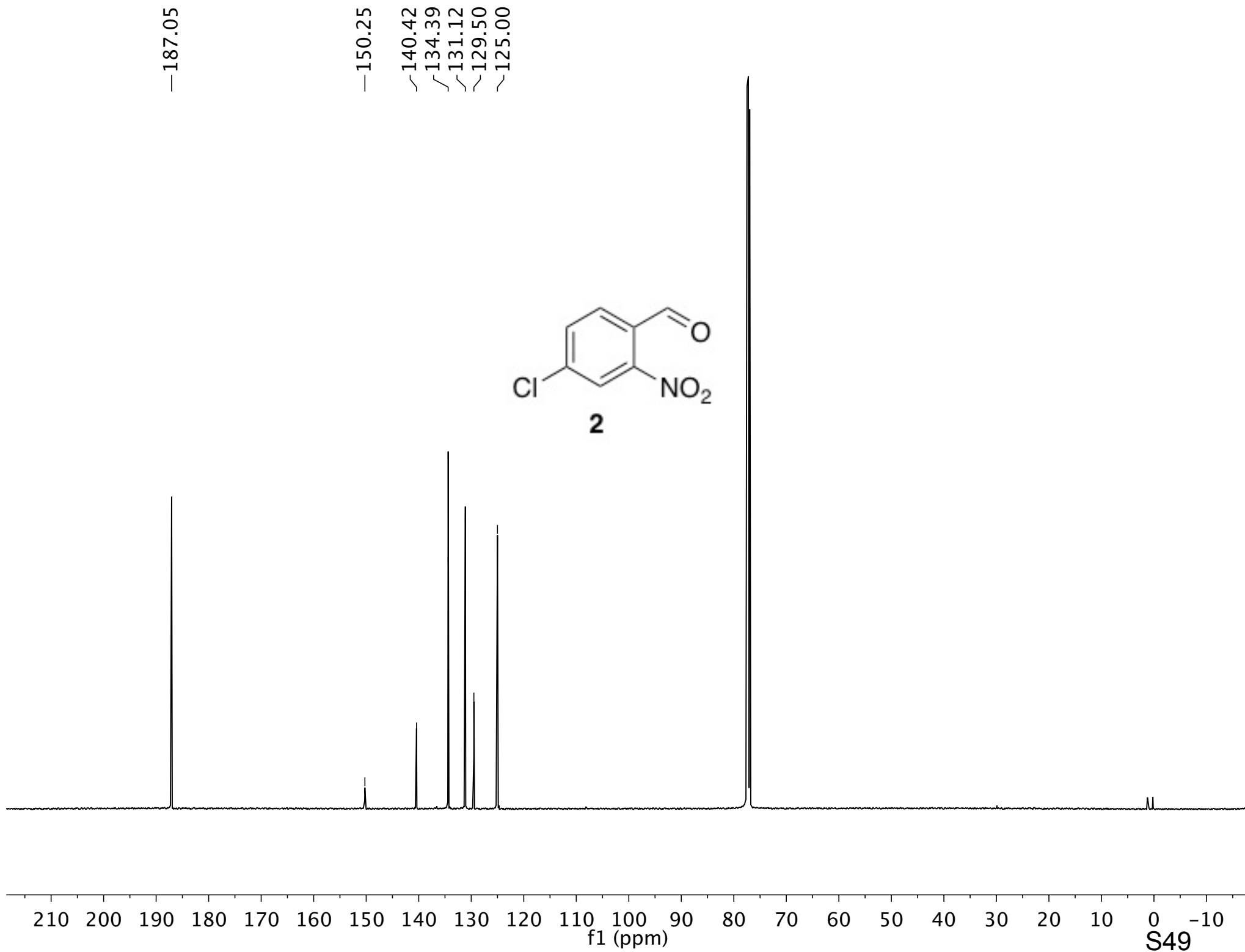


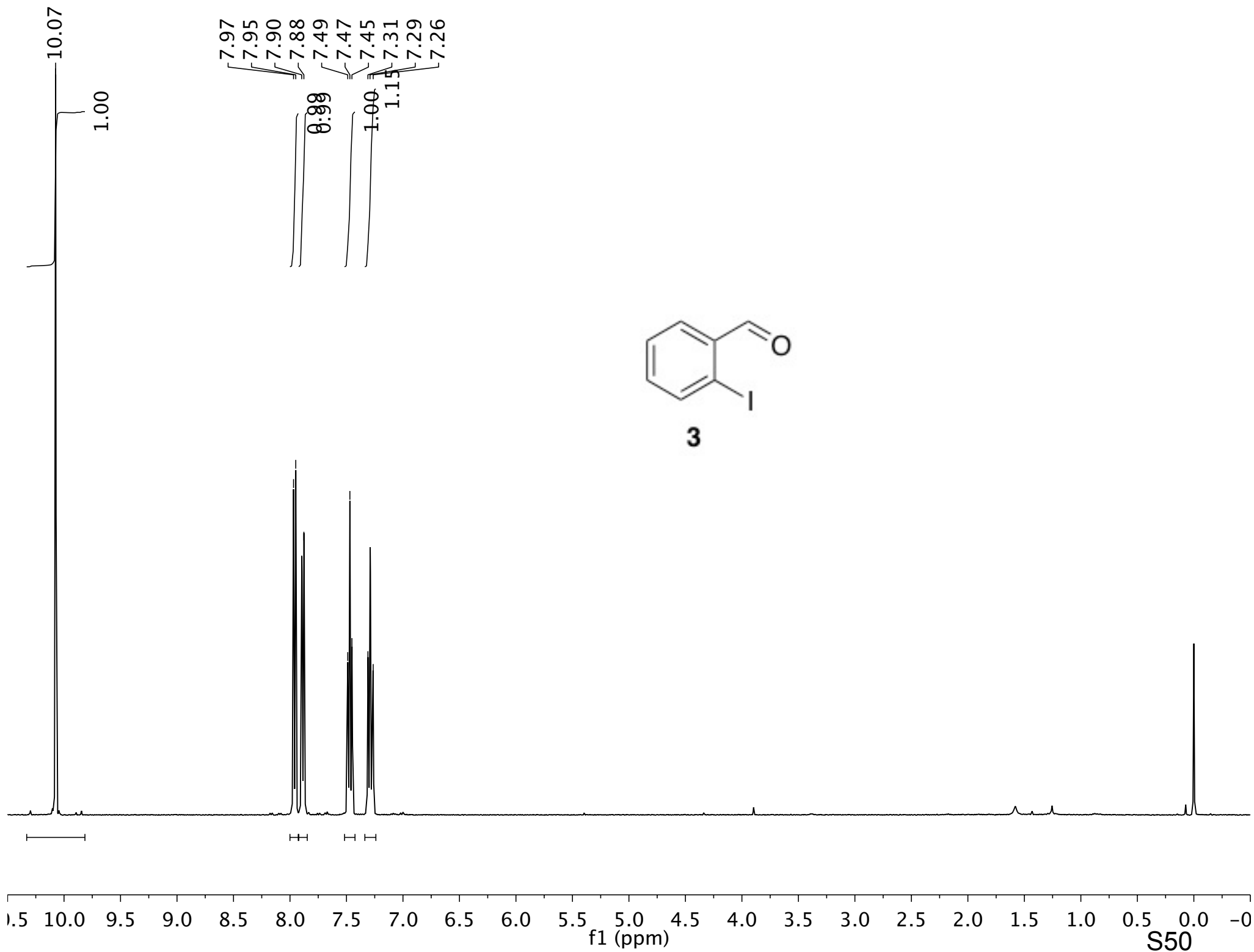








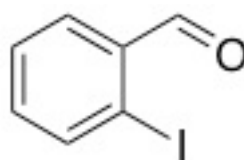




—195.79

140.67  
135.50  
135.14  
130.28  
128.74

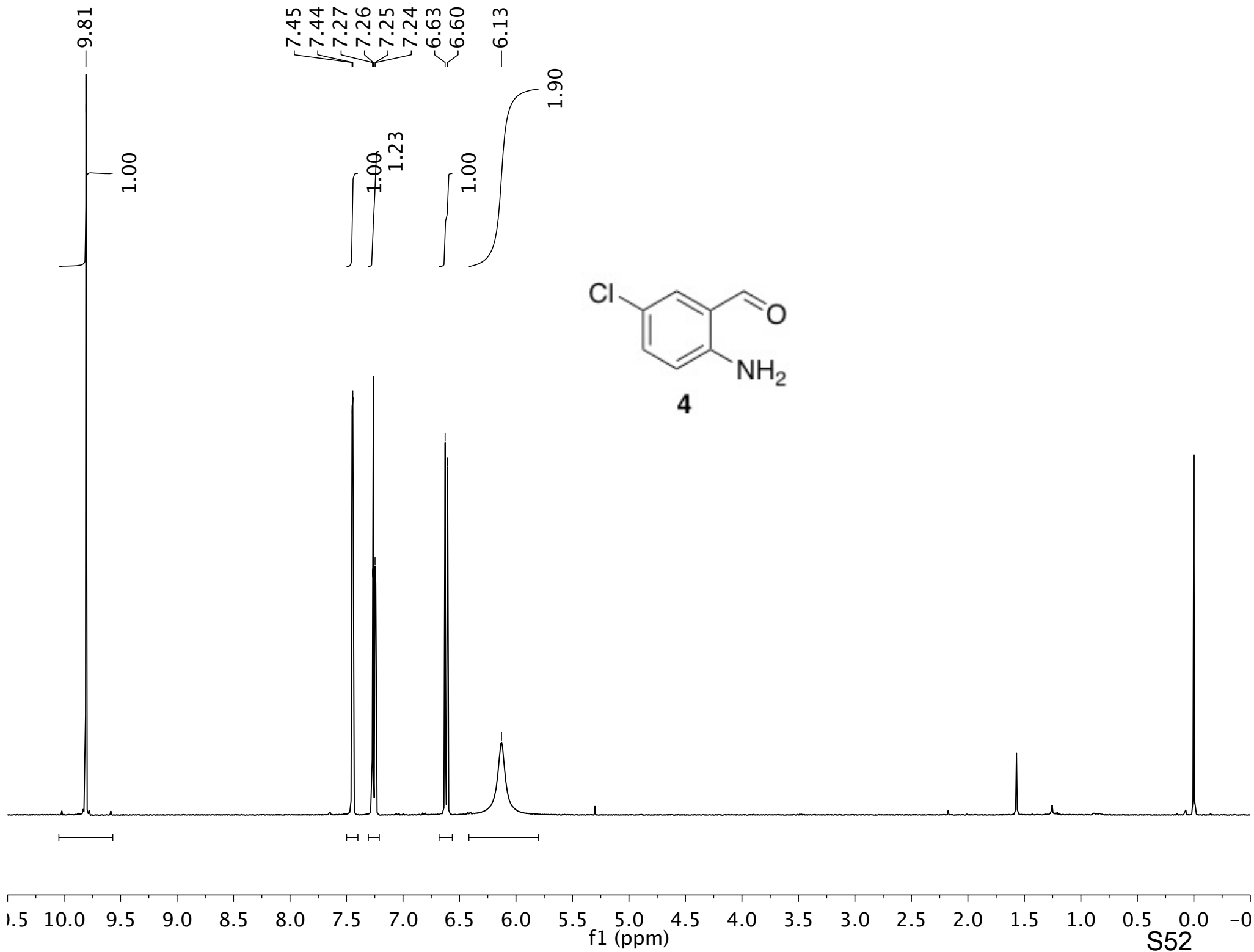
—100.73



**3**

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f1 (ppm)

S51



—192.85

—148.35

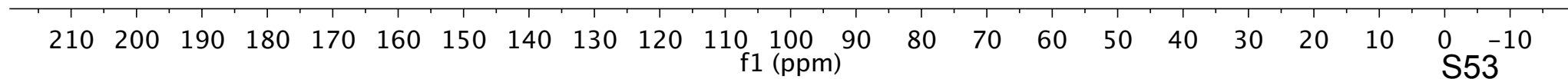
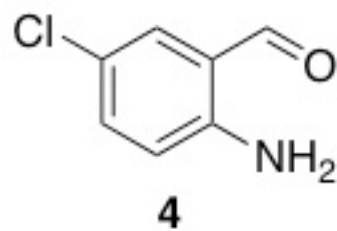
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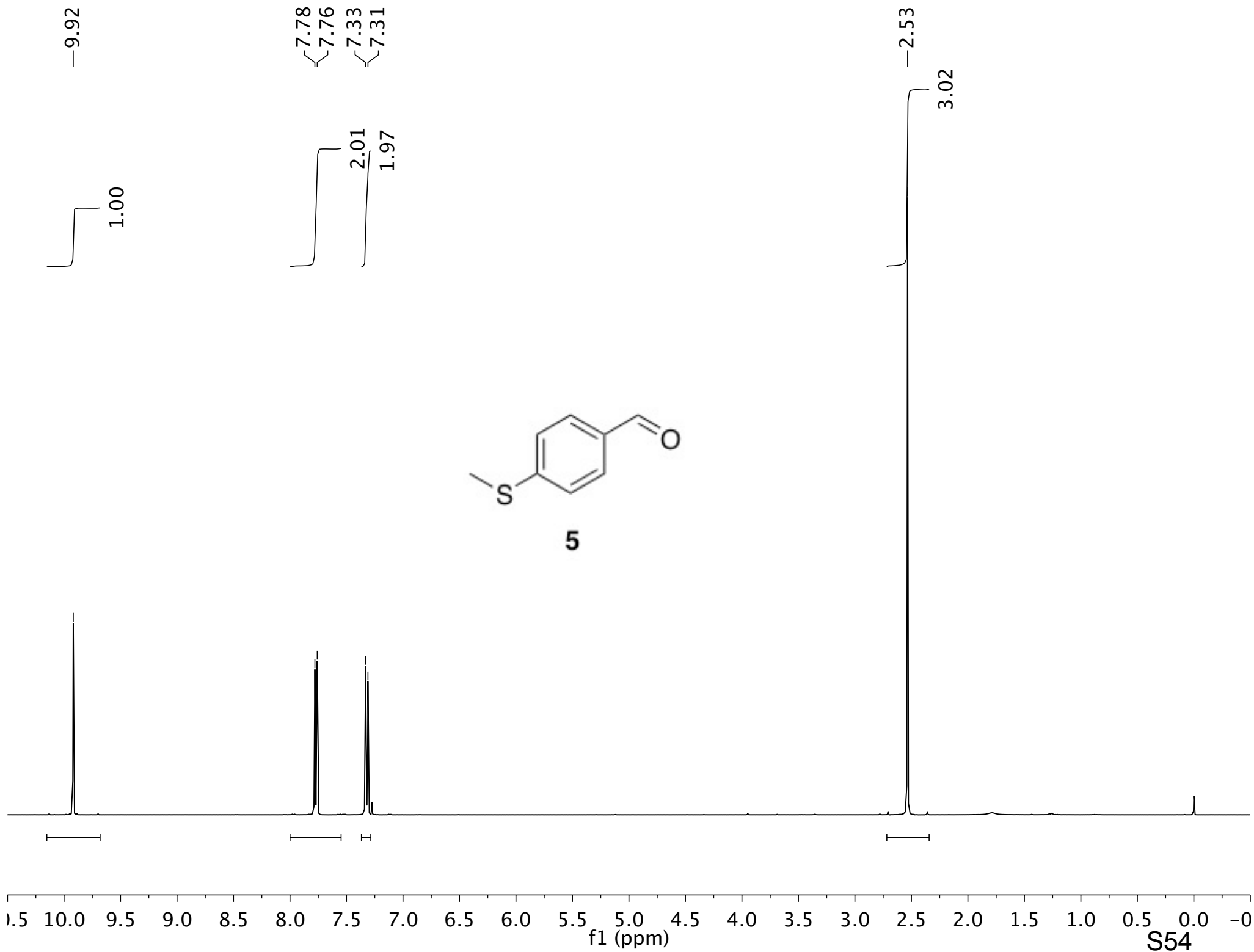
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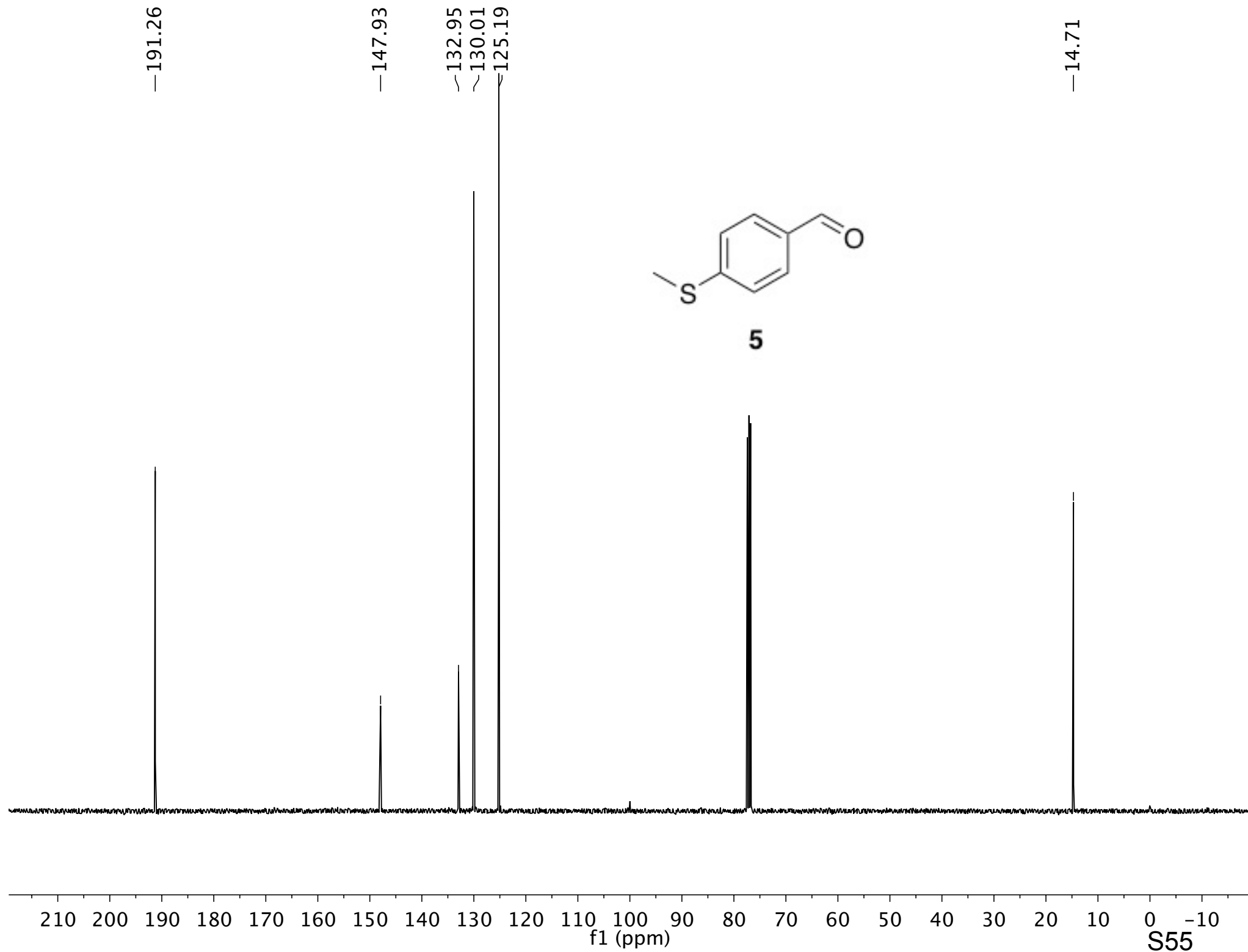
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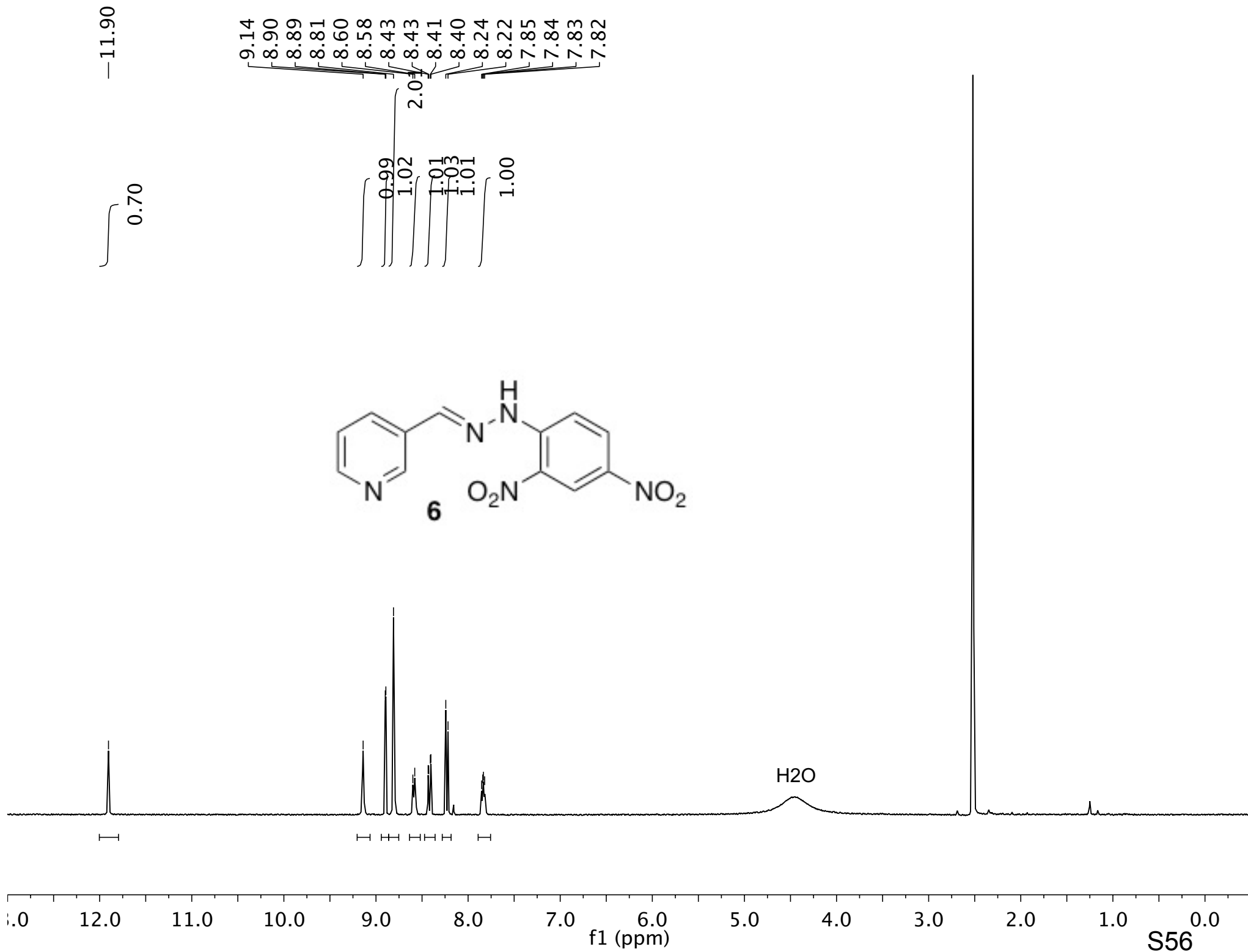
—119.31

—117.68



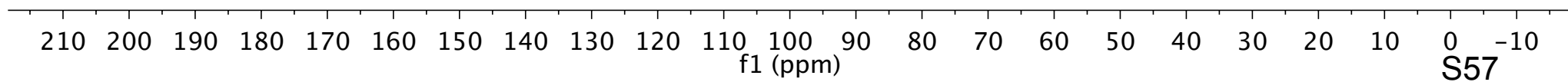
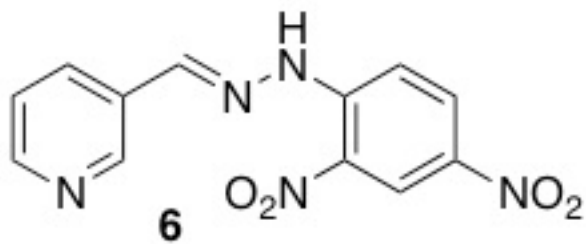






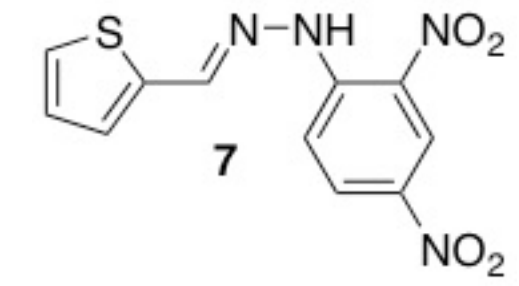


148.02  
146.13  
145.34  
144.68  
138.19  
137.69  
131.75  
130.67  
130.19  
125.86  
123.34  
117.58



11.69  
0.95

8.93  
8.87  
8.87  
8.44  
8.43  
8.42  
8.41  
7.93  
7.91  
7.77  
7.76  
7.76  
7.52  
7.51  
7.20  
7.19  
7.19  
7.18



H

H

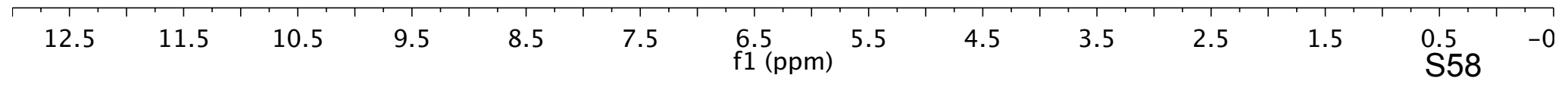
H

H

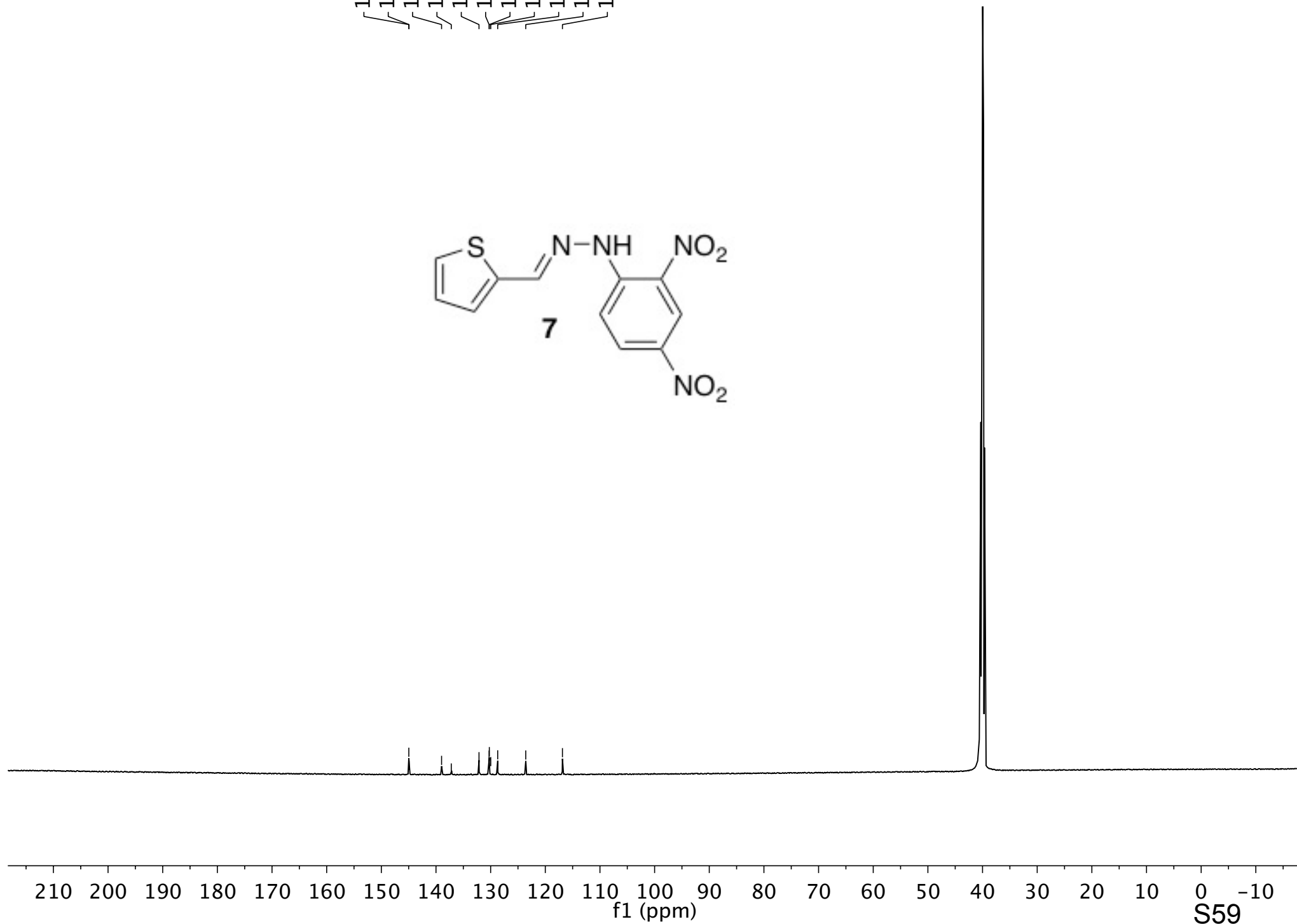
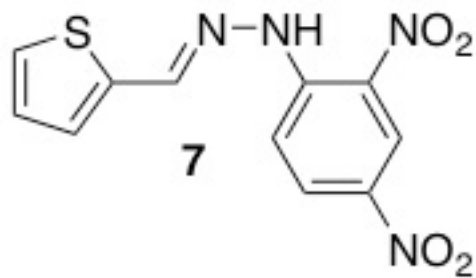
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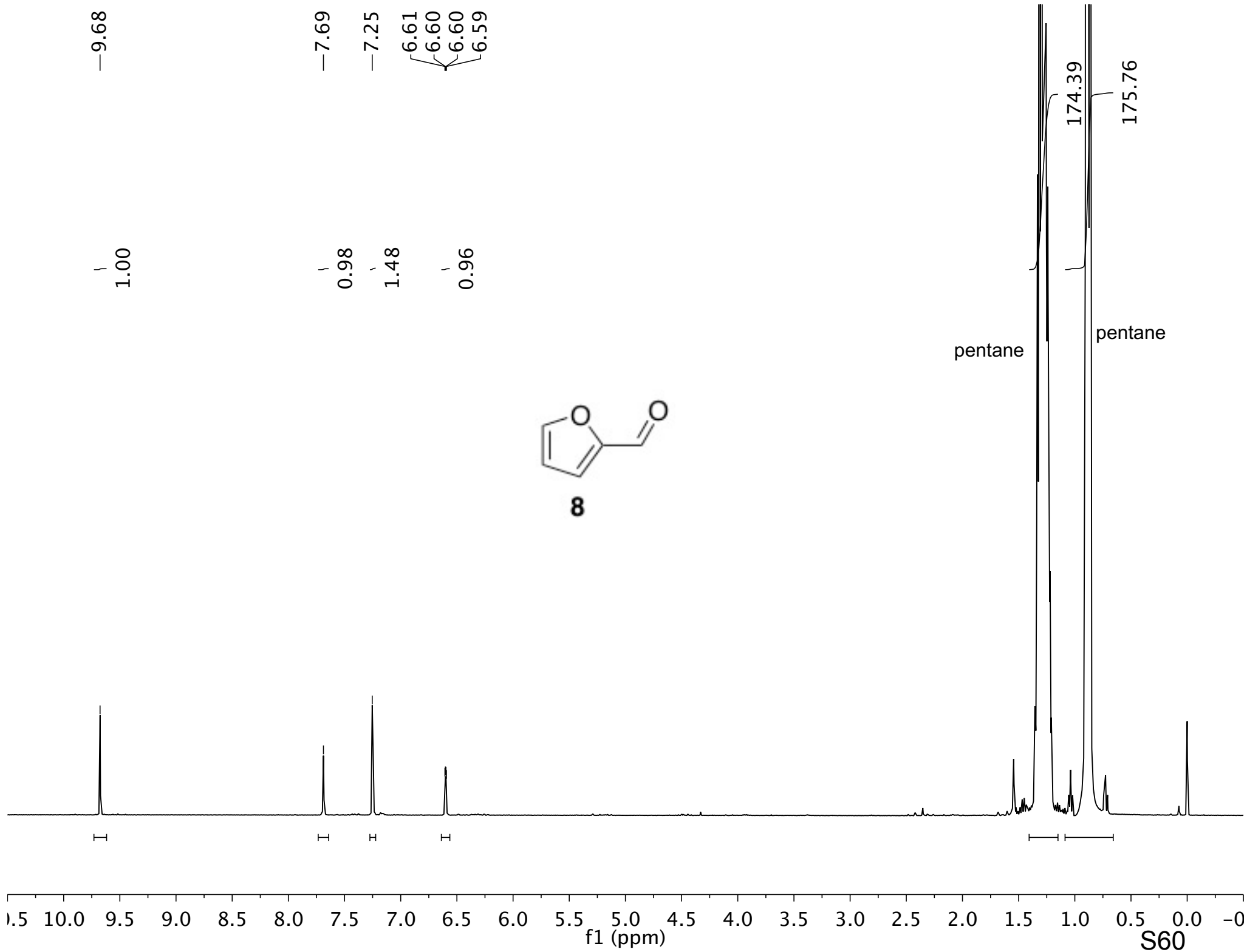
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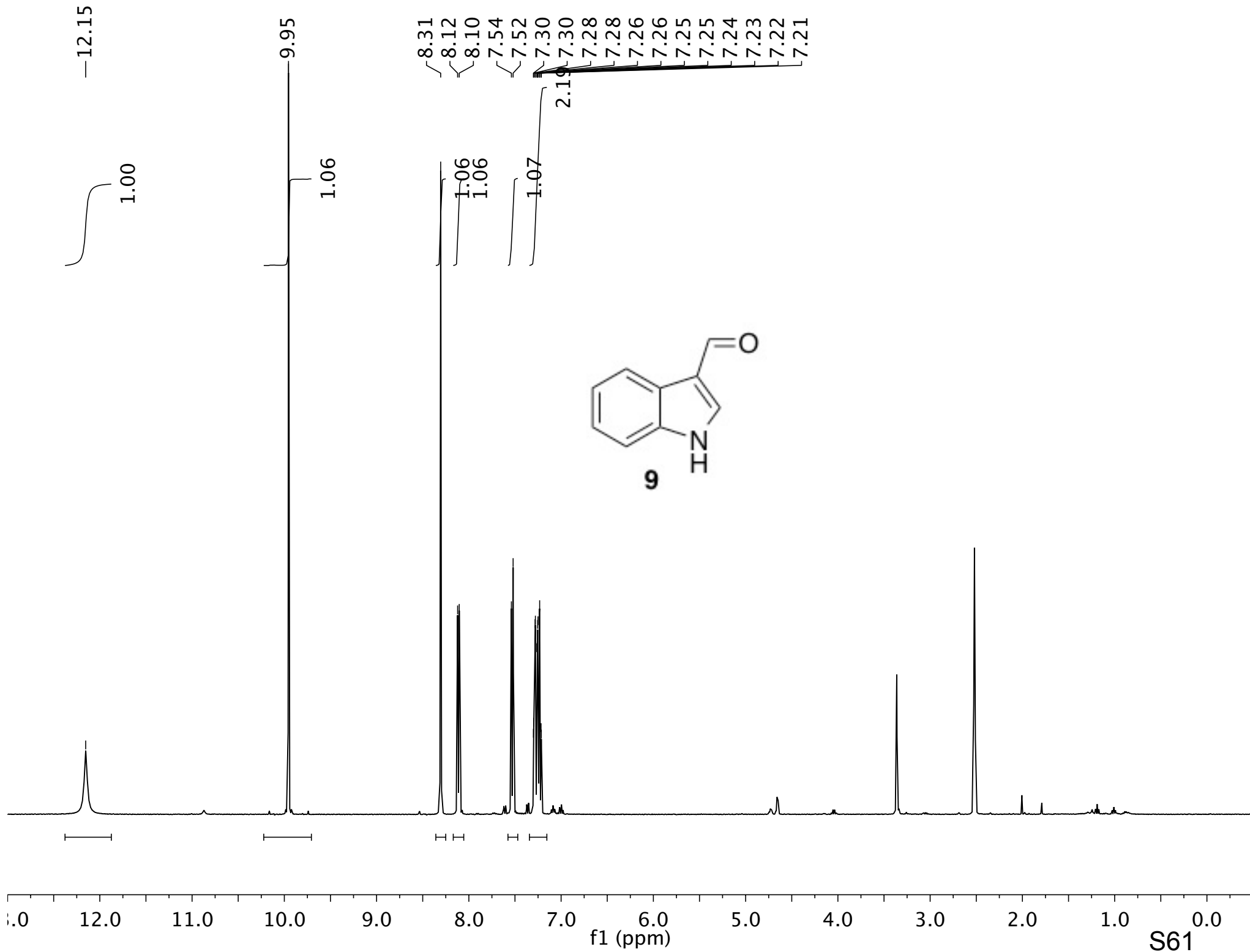
H



144.97  
144.93  
138.98  
137.20  
132.13  
130.28  
130.24  
129.98  
128.71  
123.58  
116.86







—185.43

138.94

137.51

124.58

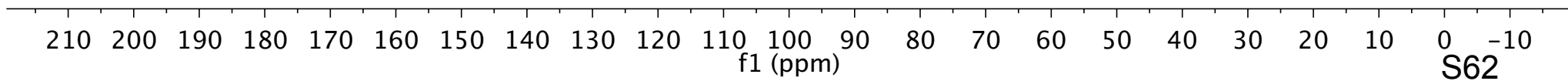
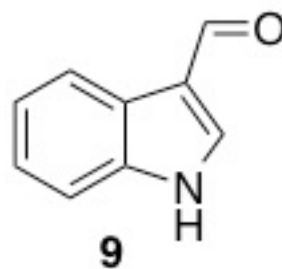
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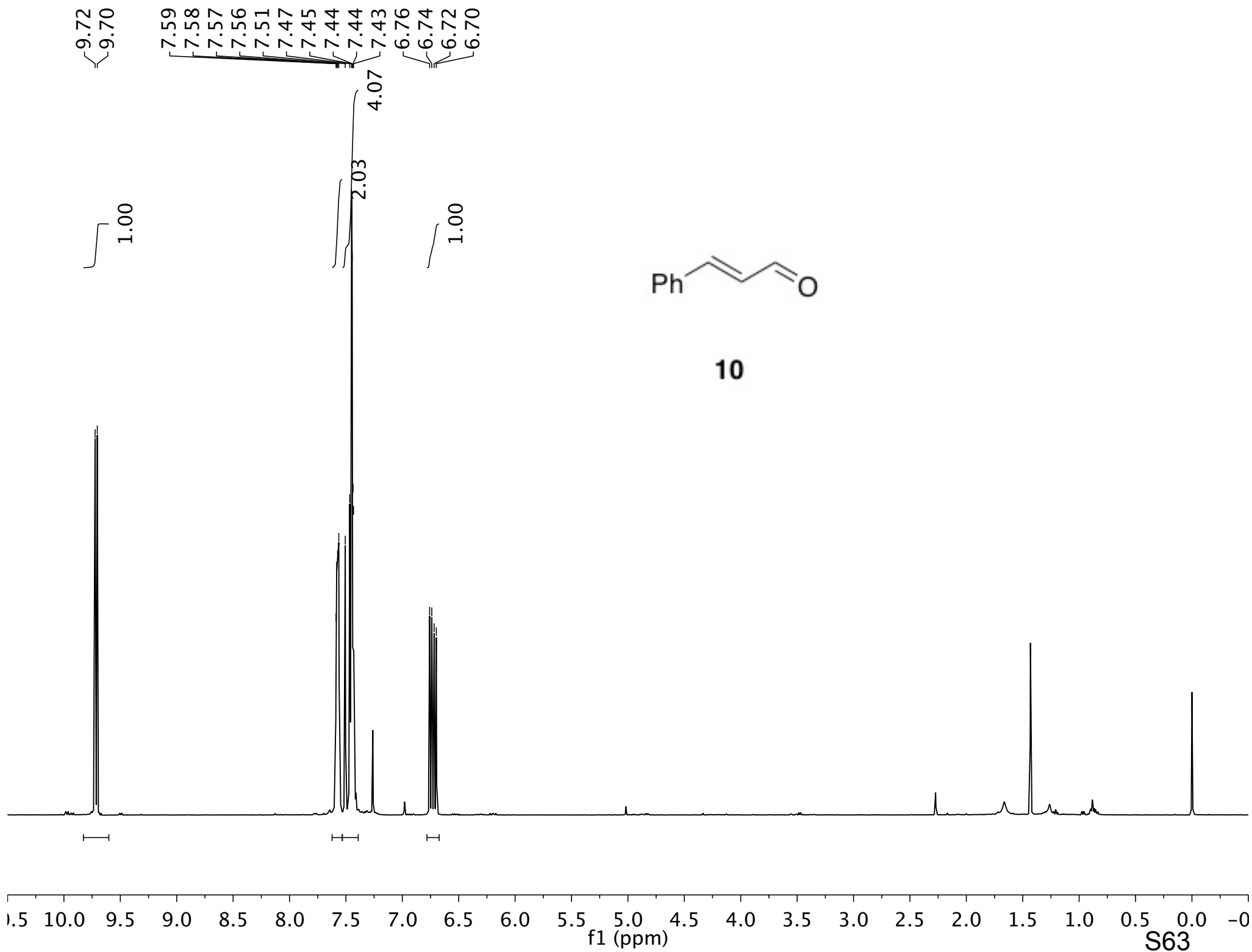
122.59

121.29

118.63

112.89





—193.74

—152.83

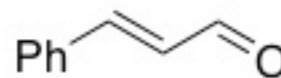
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128.52

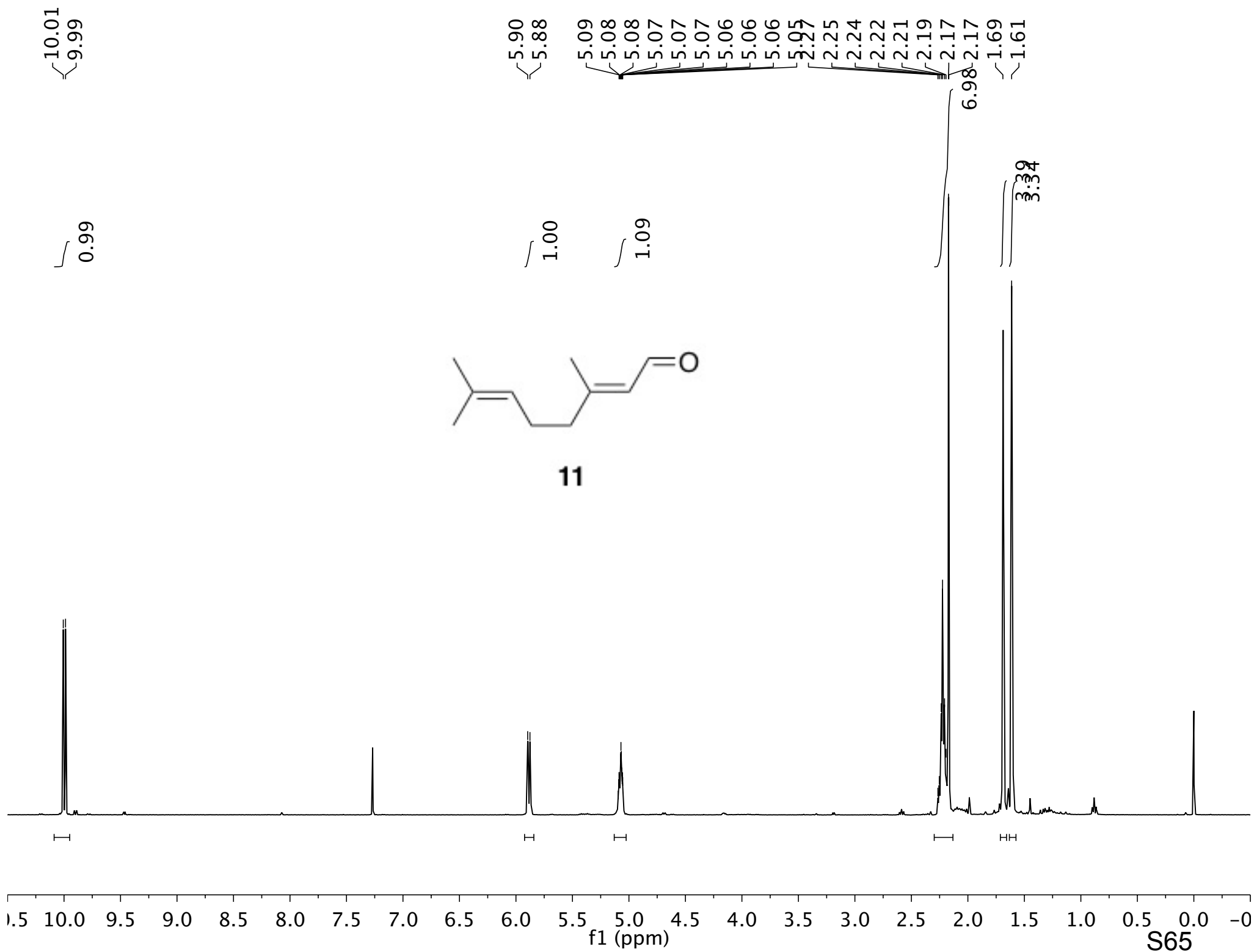


**10**

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10  
f1 (ppm)

S64





—191.33

—163.86

~132.95

~127.44

~122.57

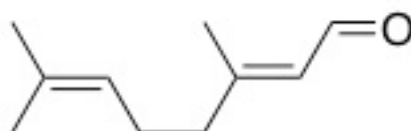
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—25.75

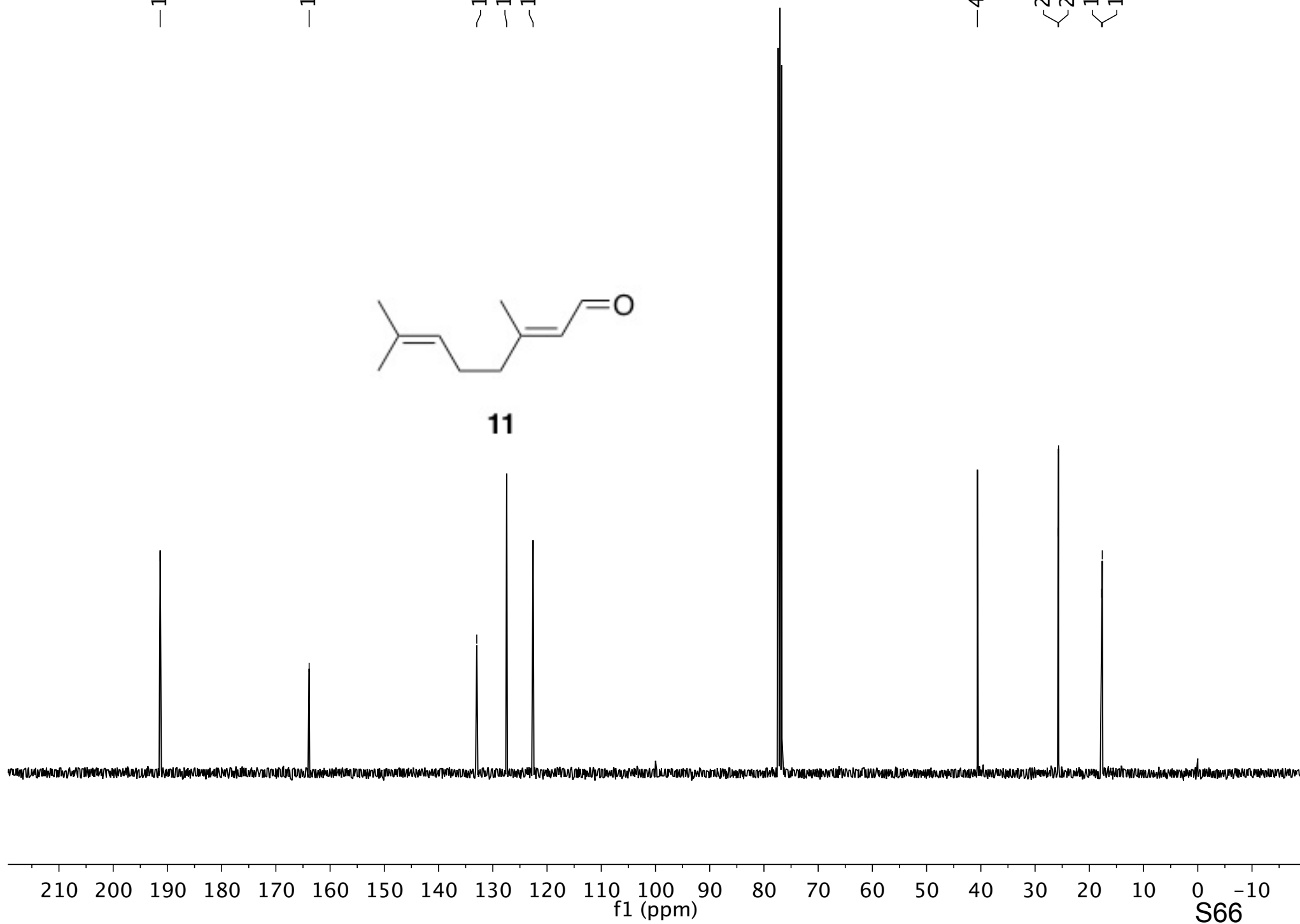
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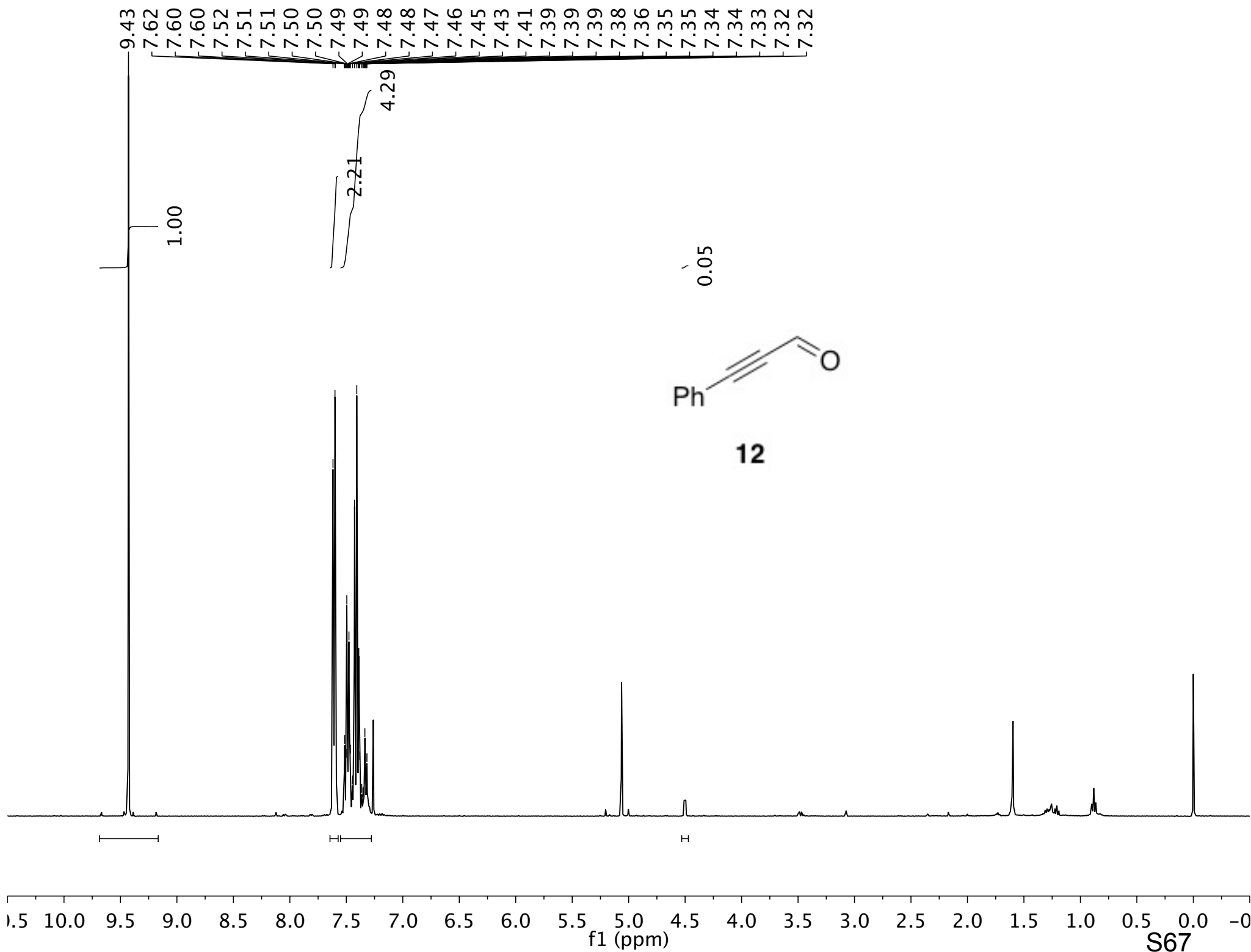
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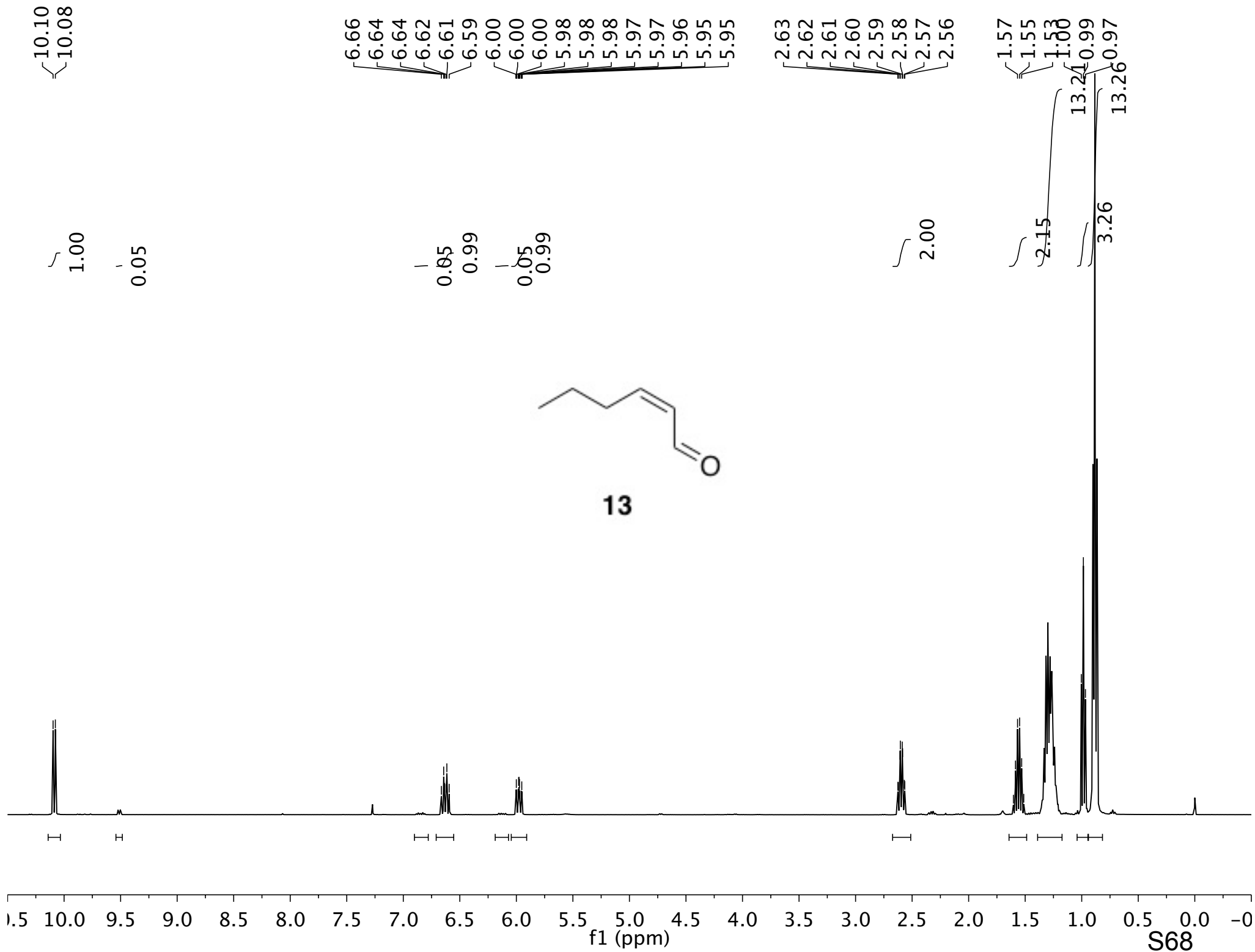
—17.61



**11**





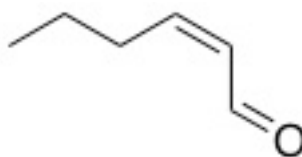


—190.93

—153.14

—130.39

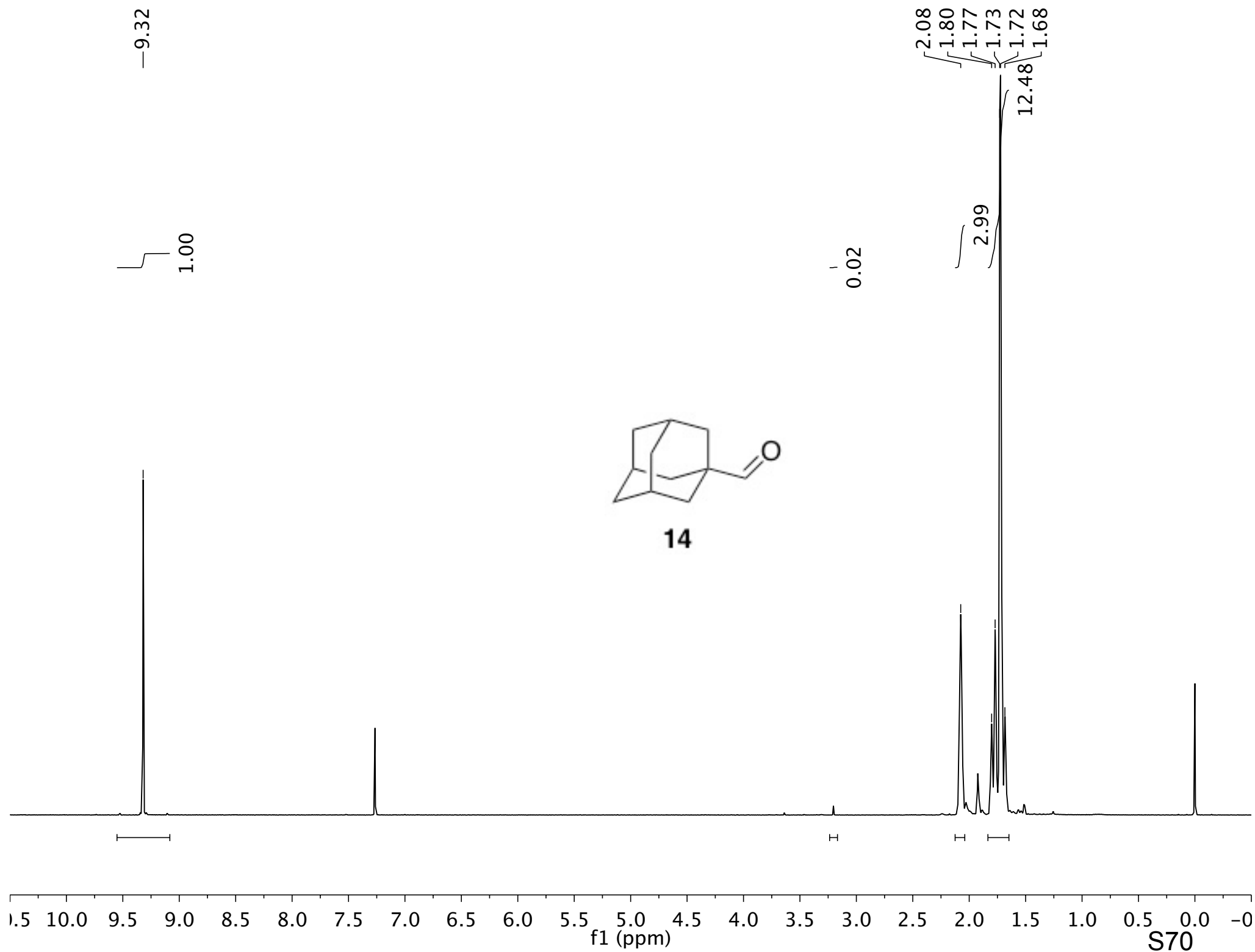
29.87  
22.41  
13.55

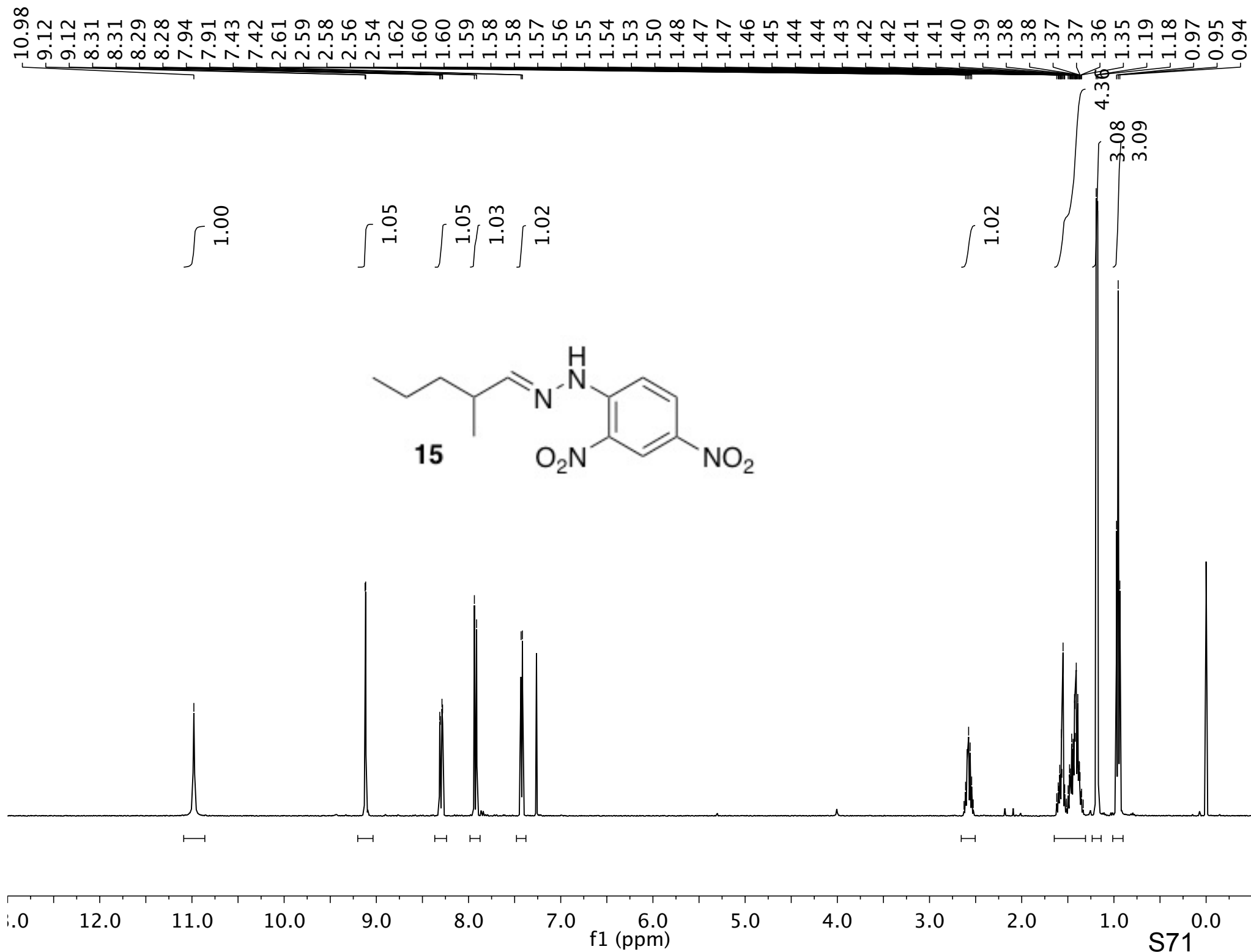


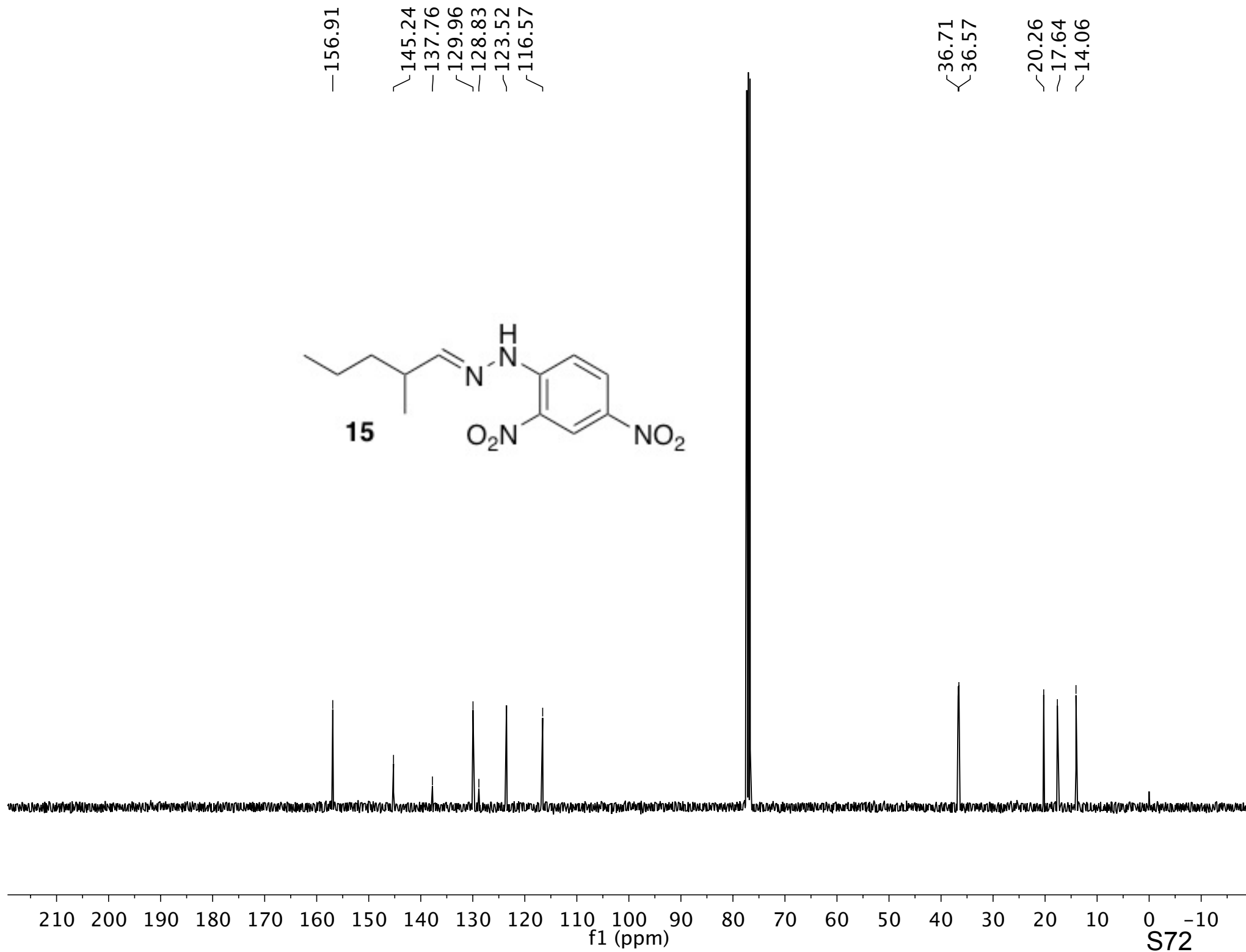
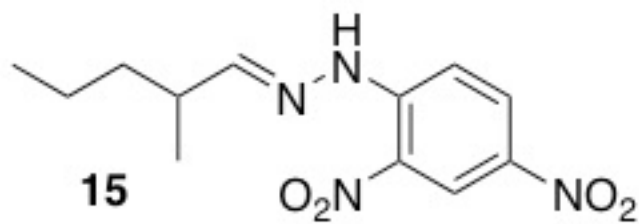
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f1 (ppm)

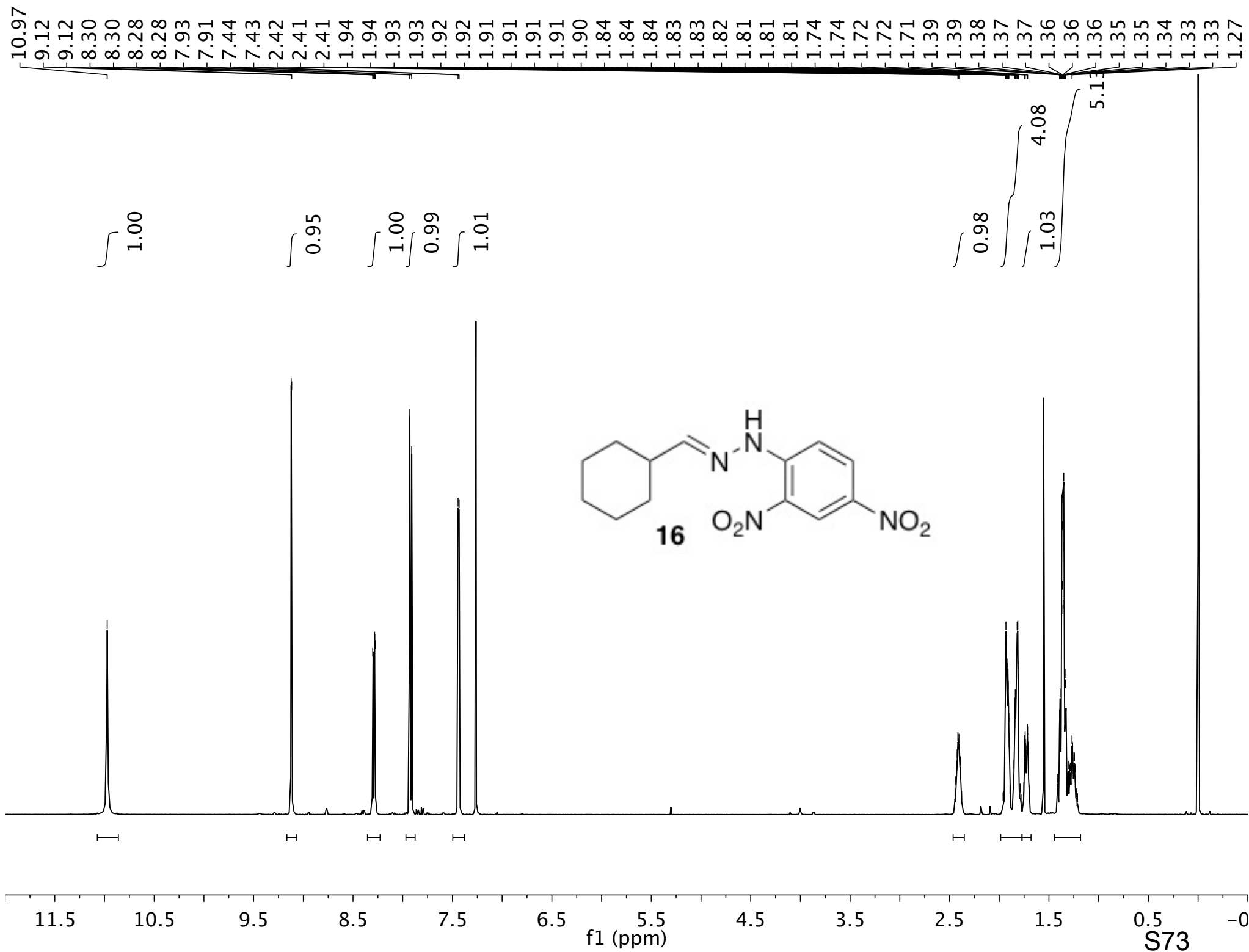
S69

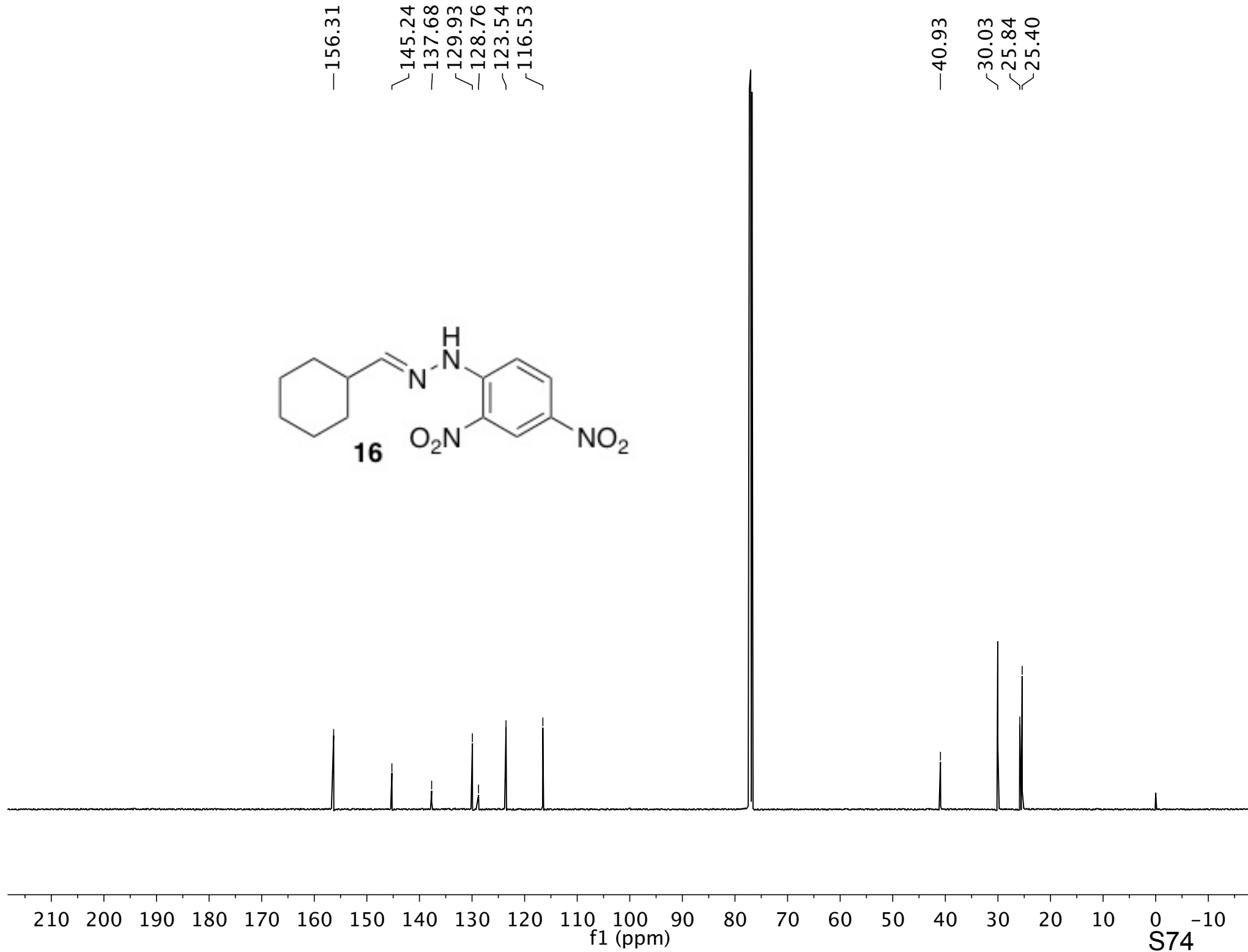
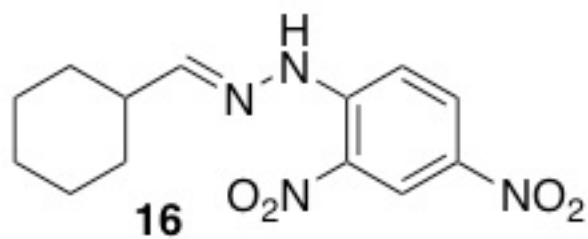


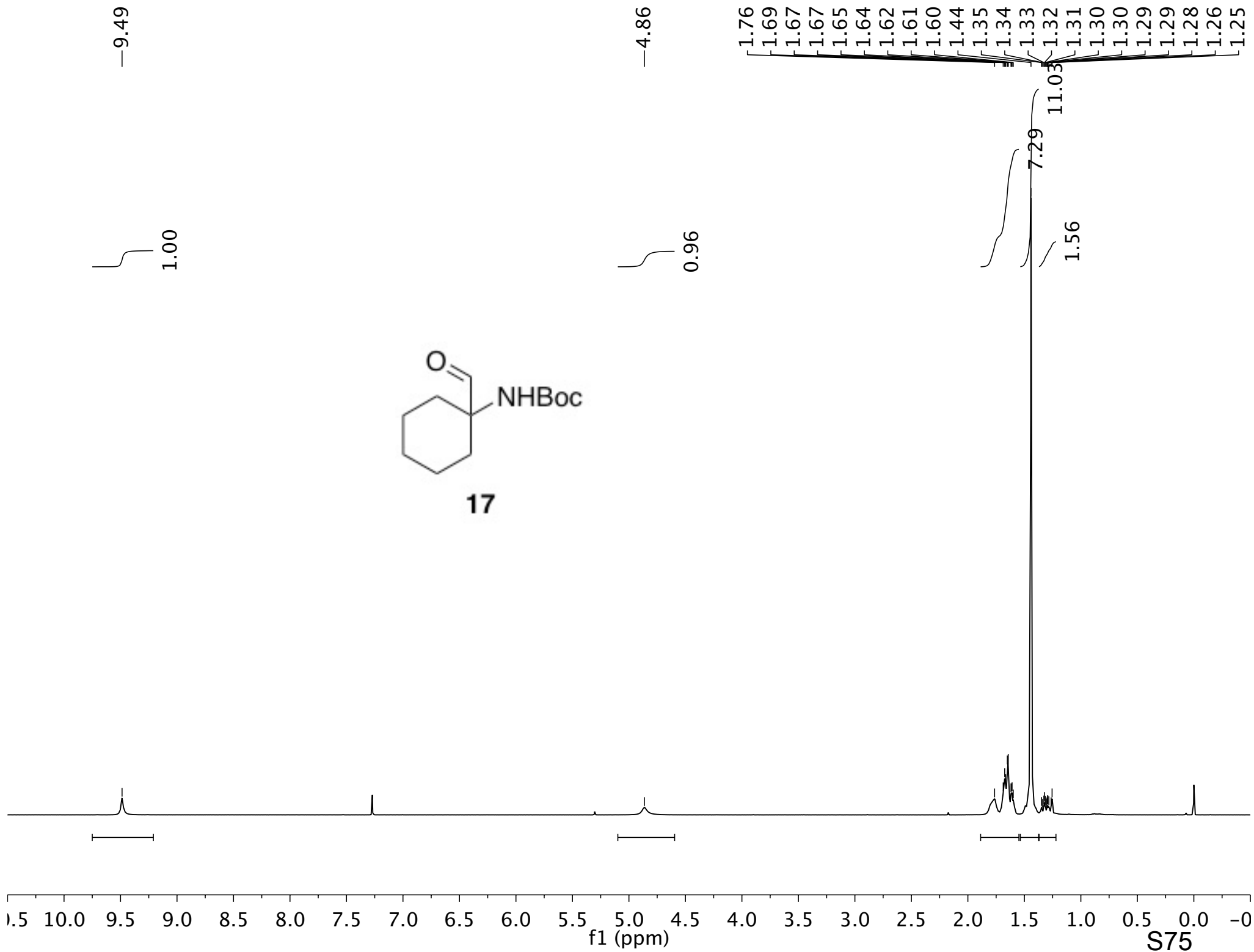


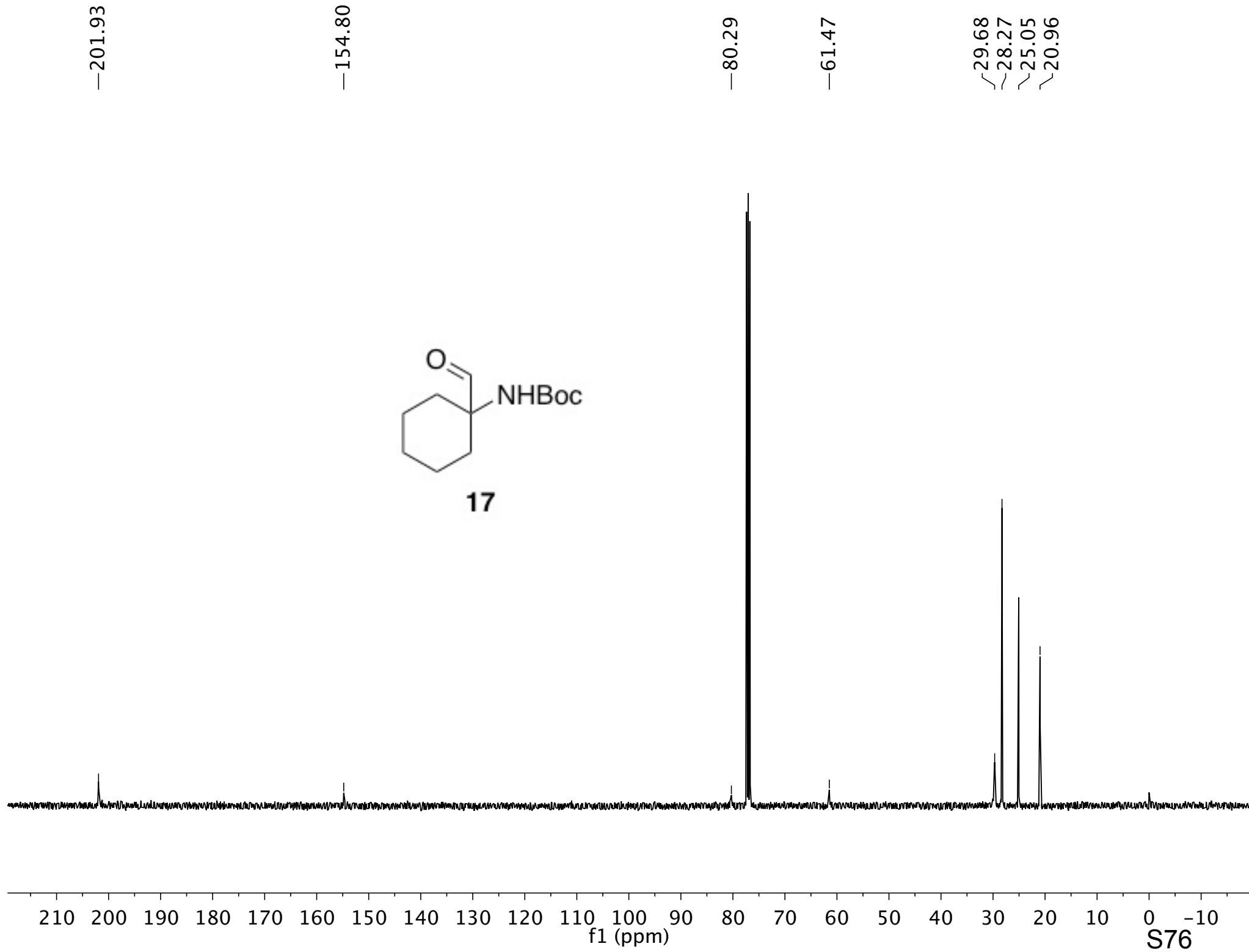


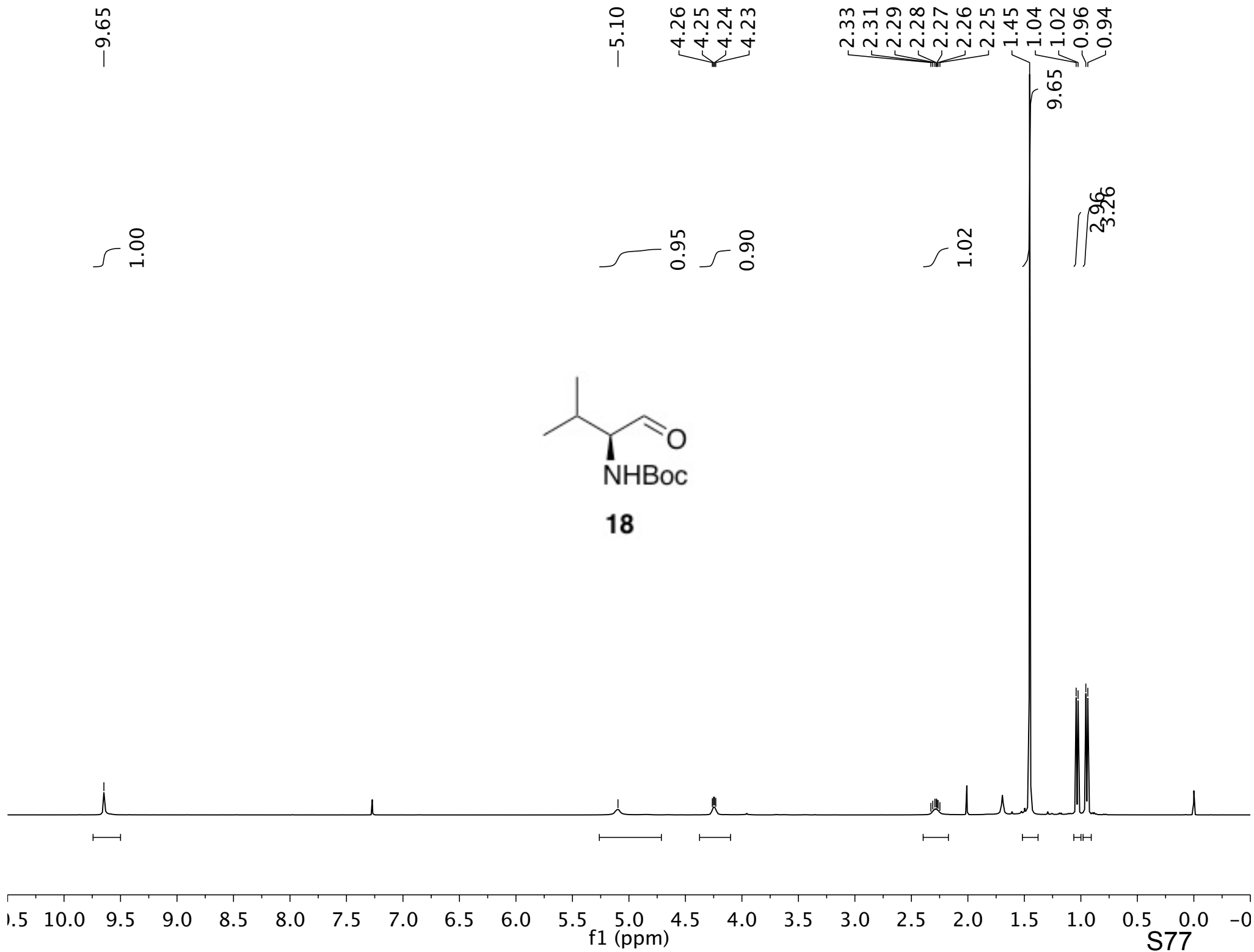


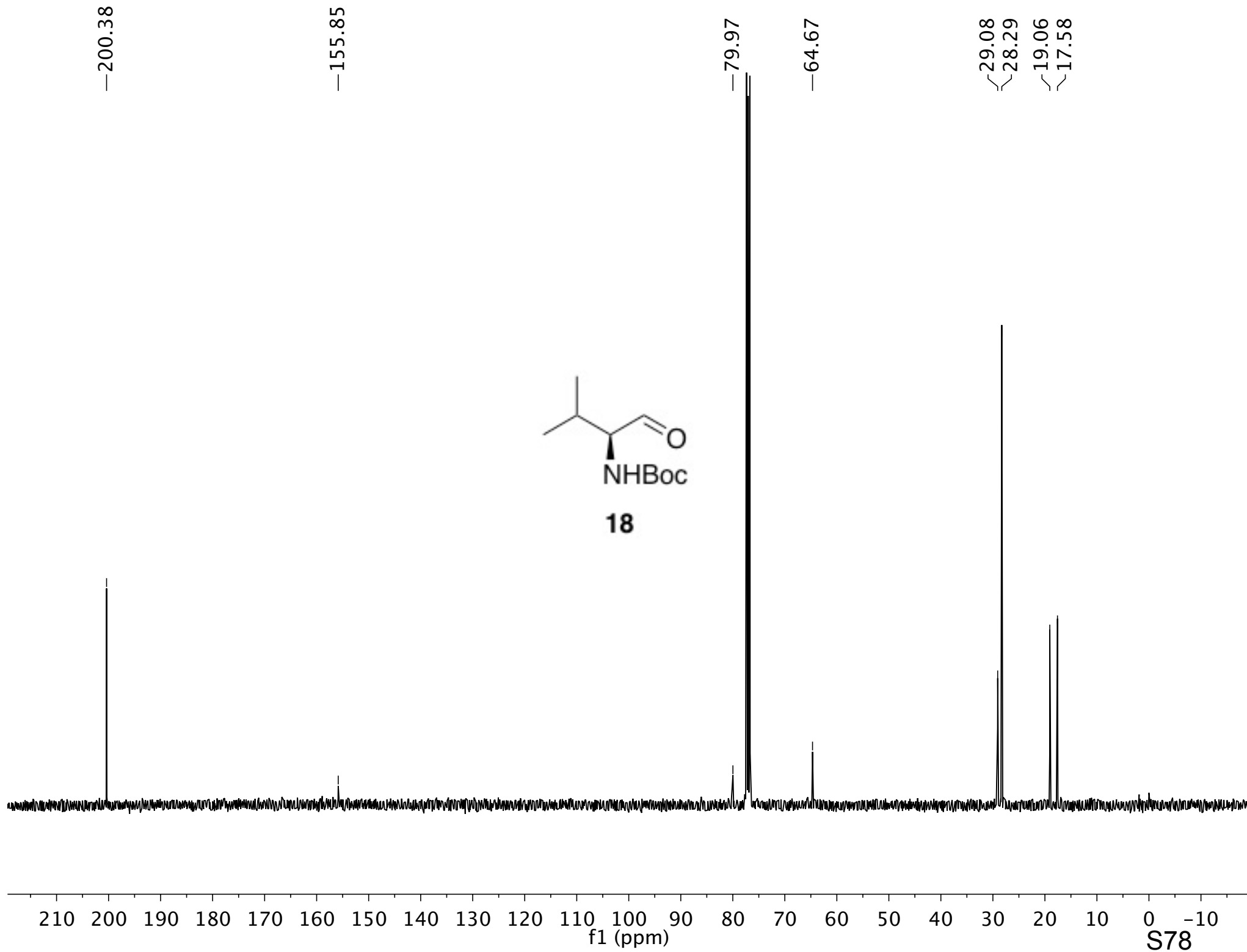


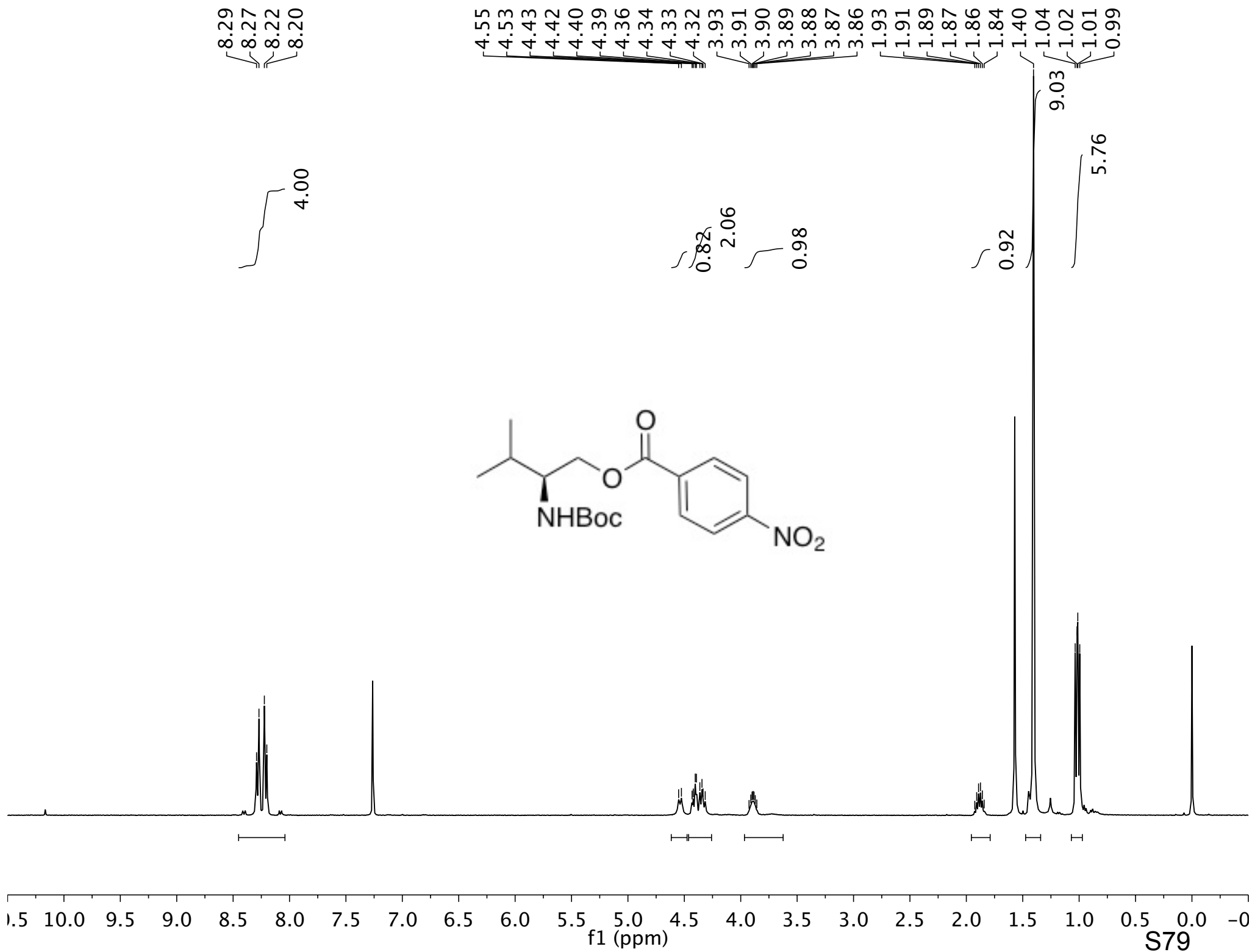


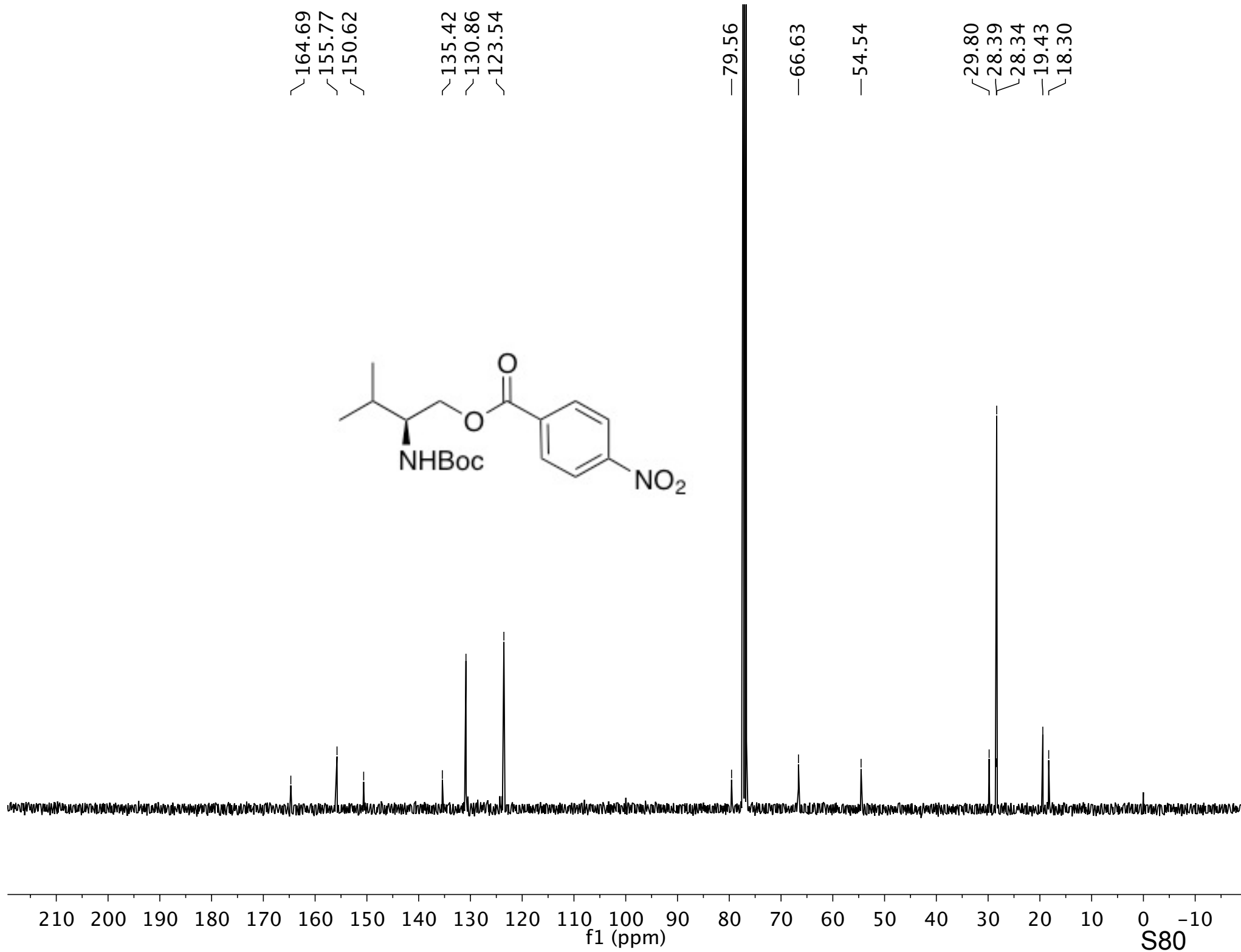




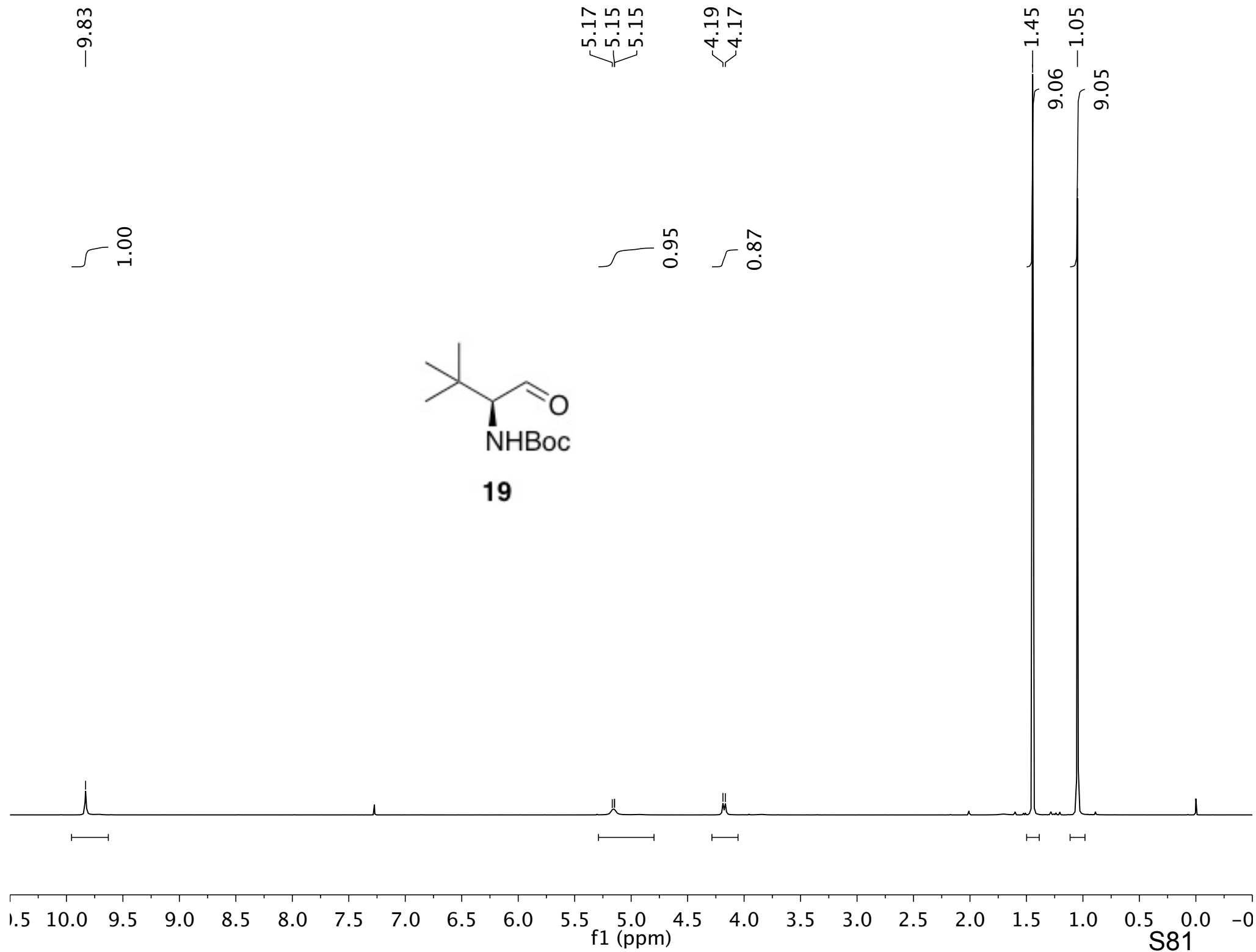


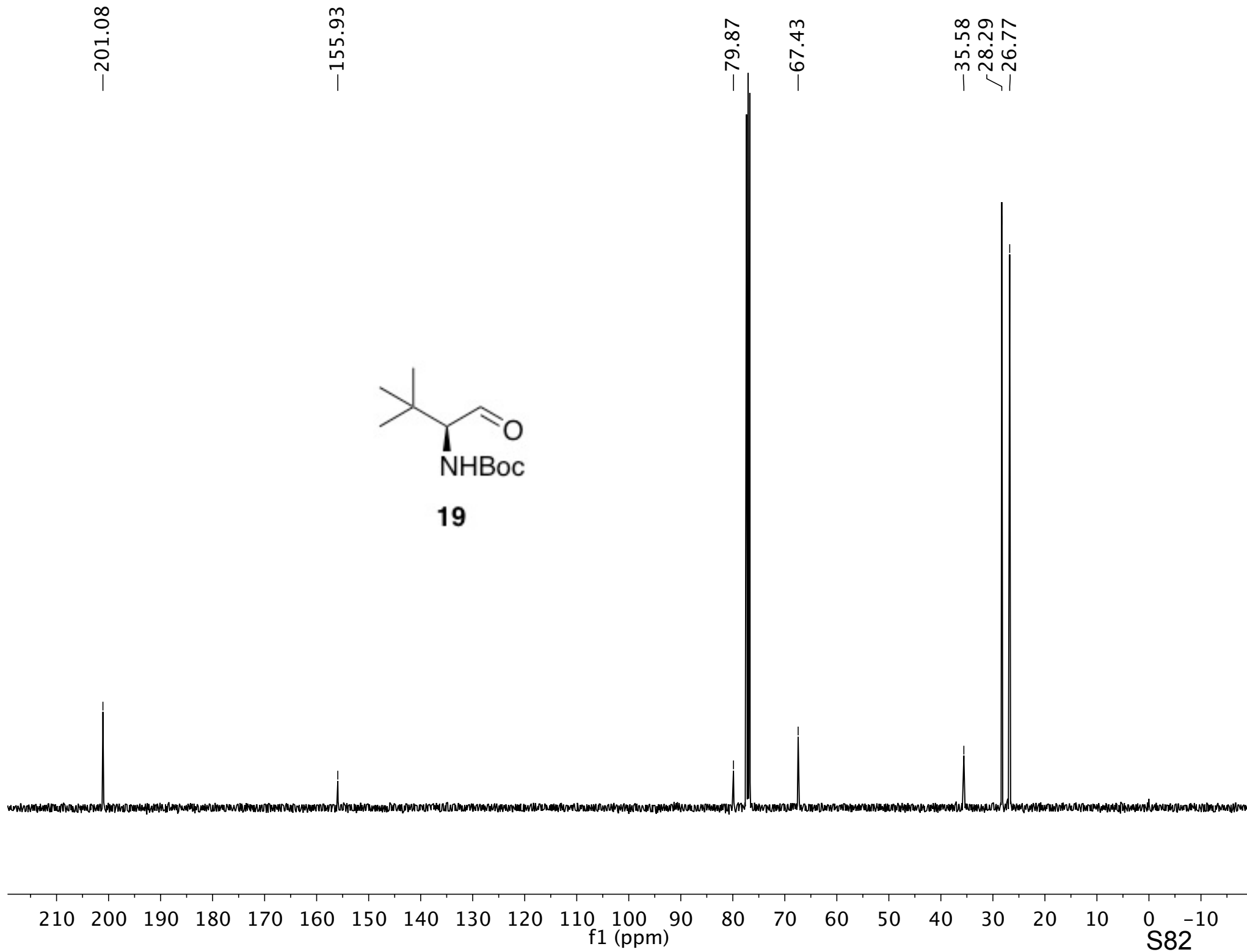


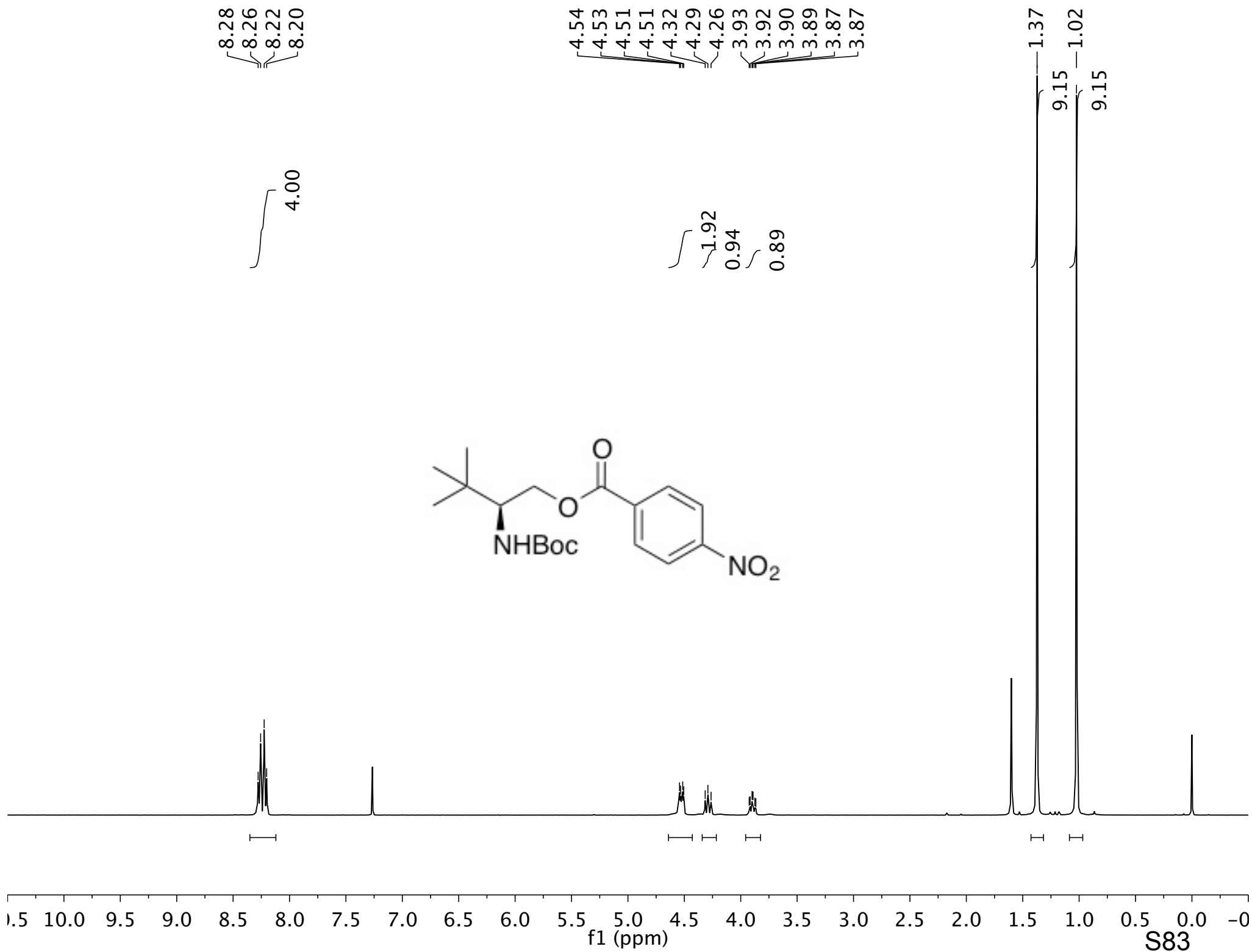












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155.97  
150.61

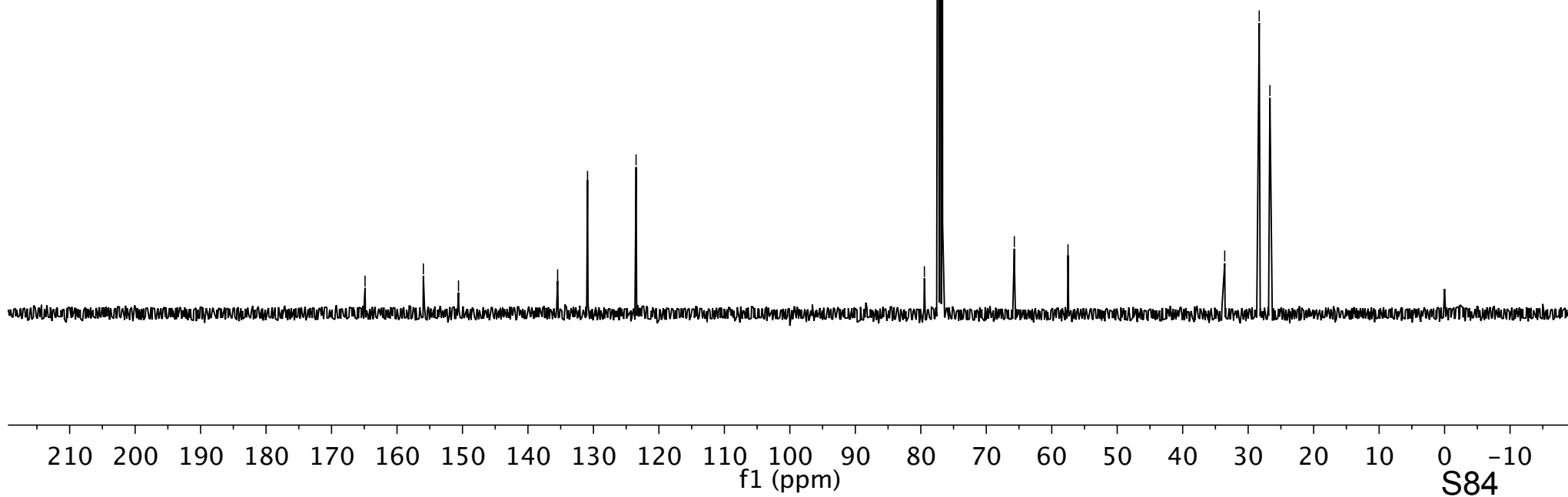
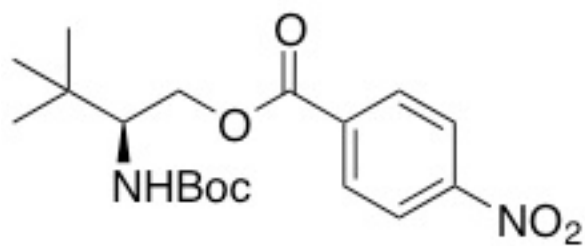
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123.48

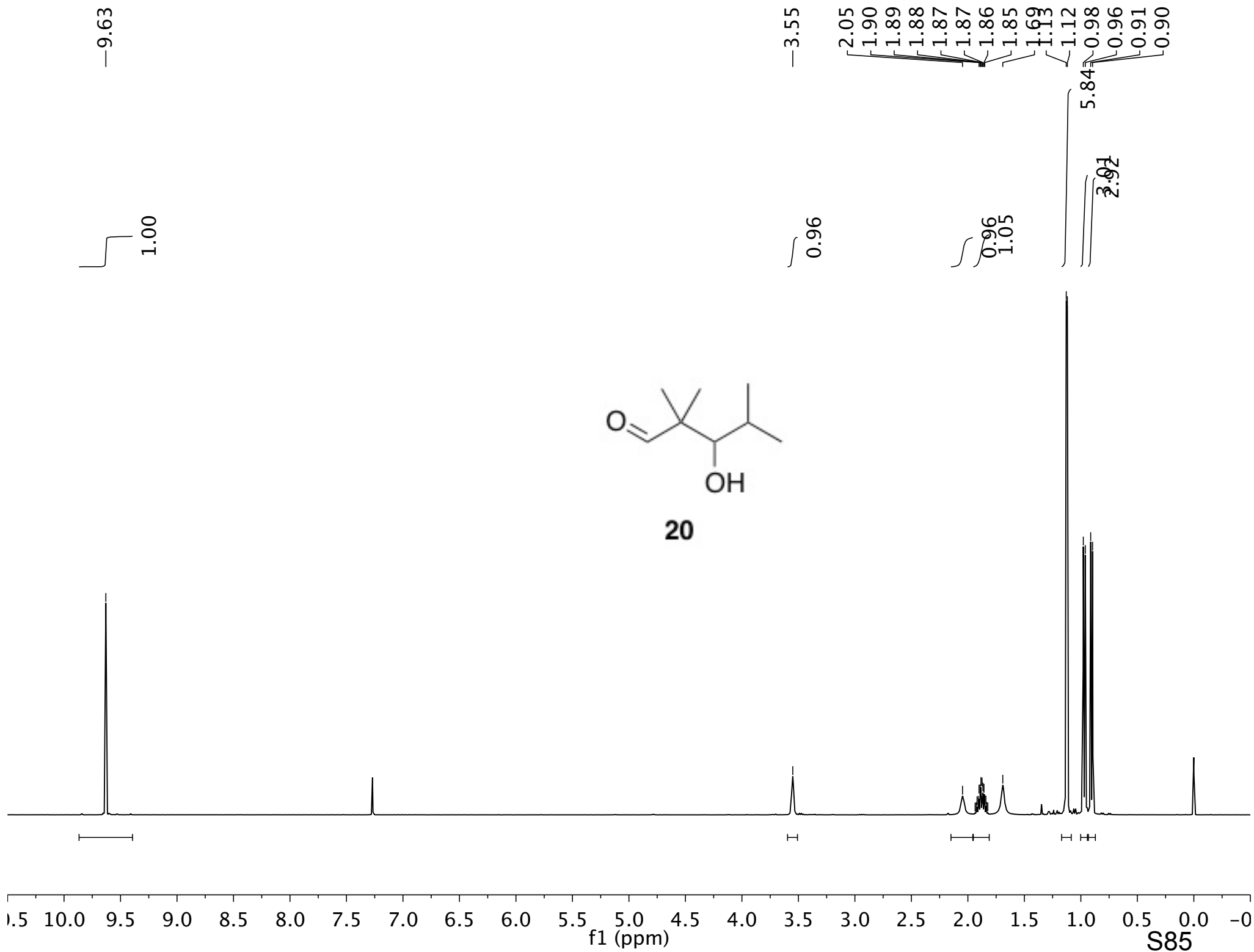
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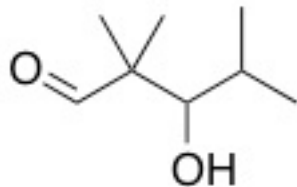
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57.52

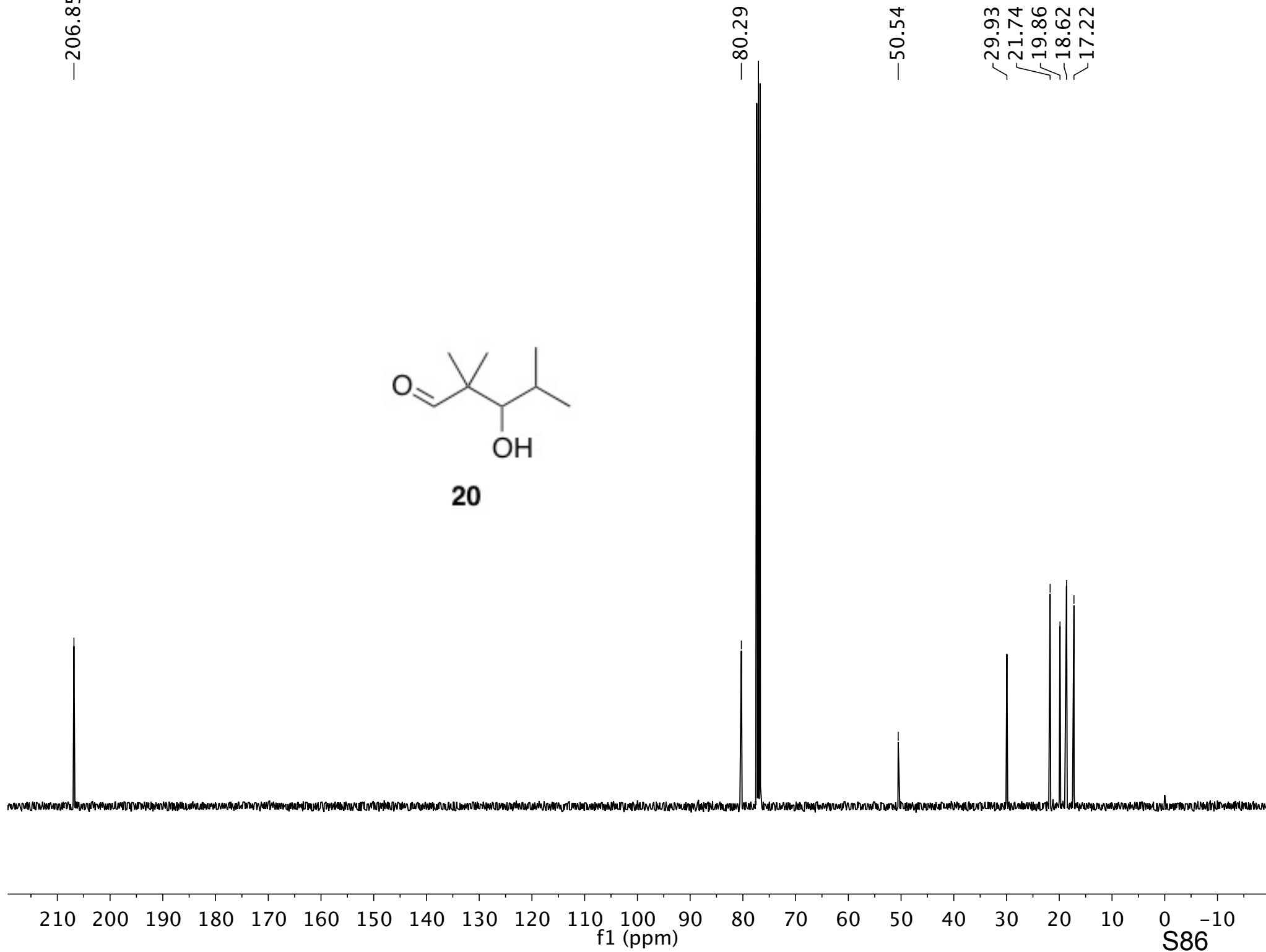
33.58  
28.31  
26.68







20



7.99  
7.97  
7.62  
7.60  
7.58  
7.51  
7.49  
7.47

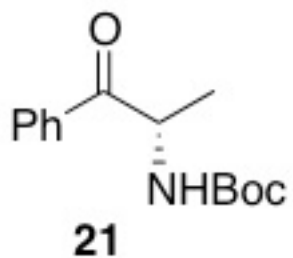
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5.33  
5.32  
5.30  
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1.46  
1.41  
1.39

2.00  
1.00  
1.99

0.88  
1.00

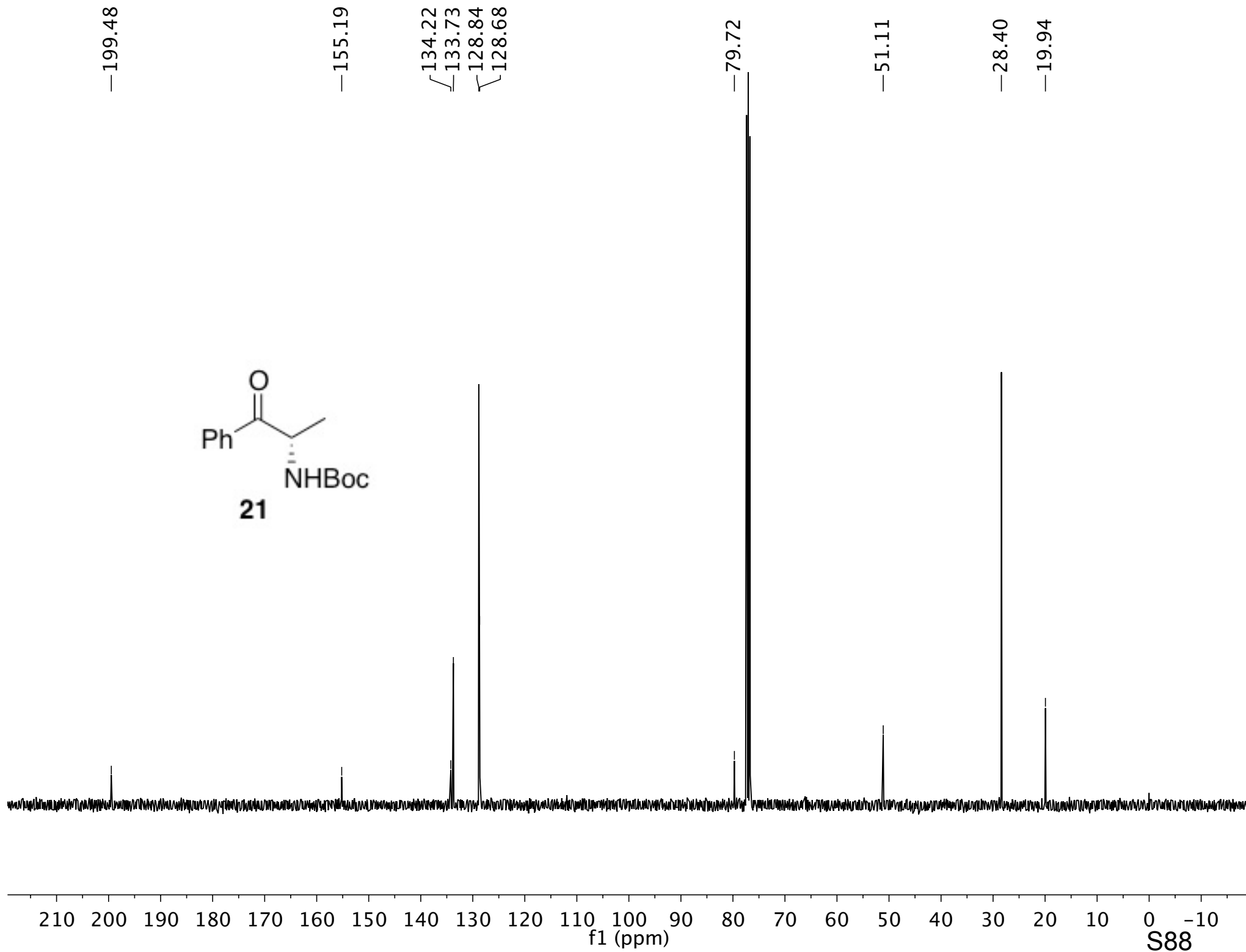
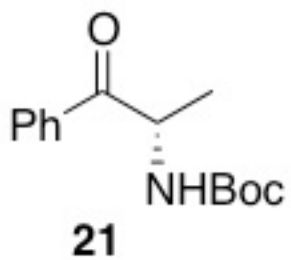
3.02  
9.02



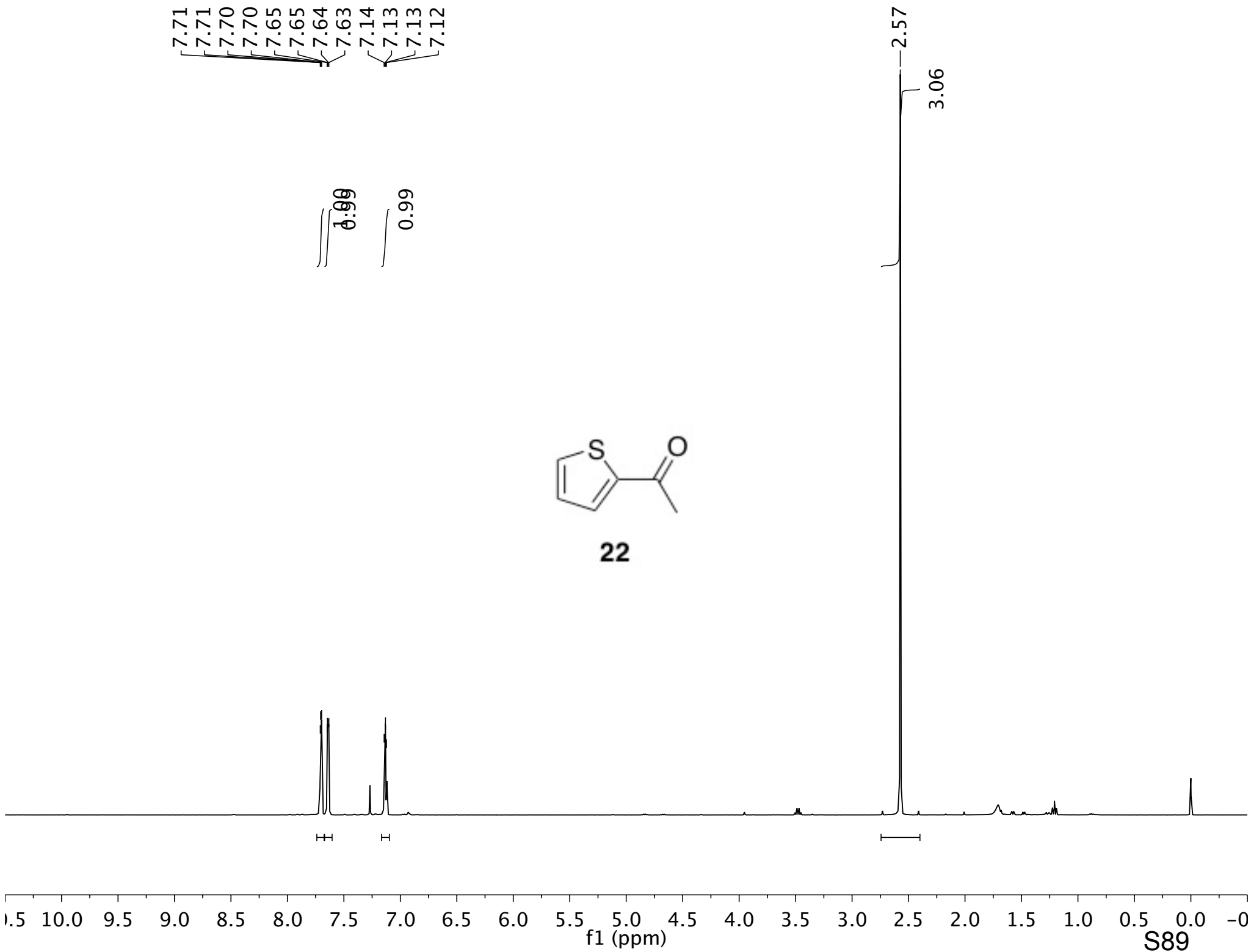
1.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

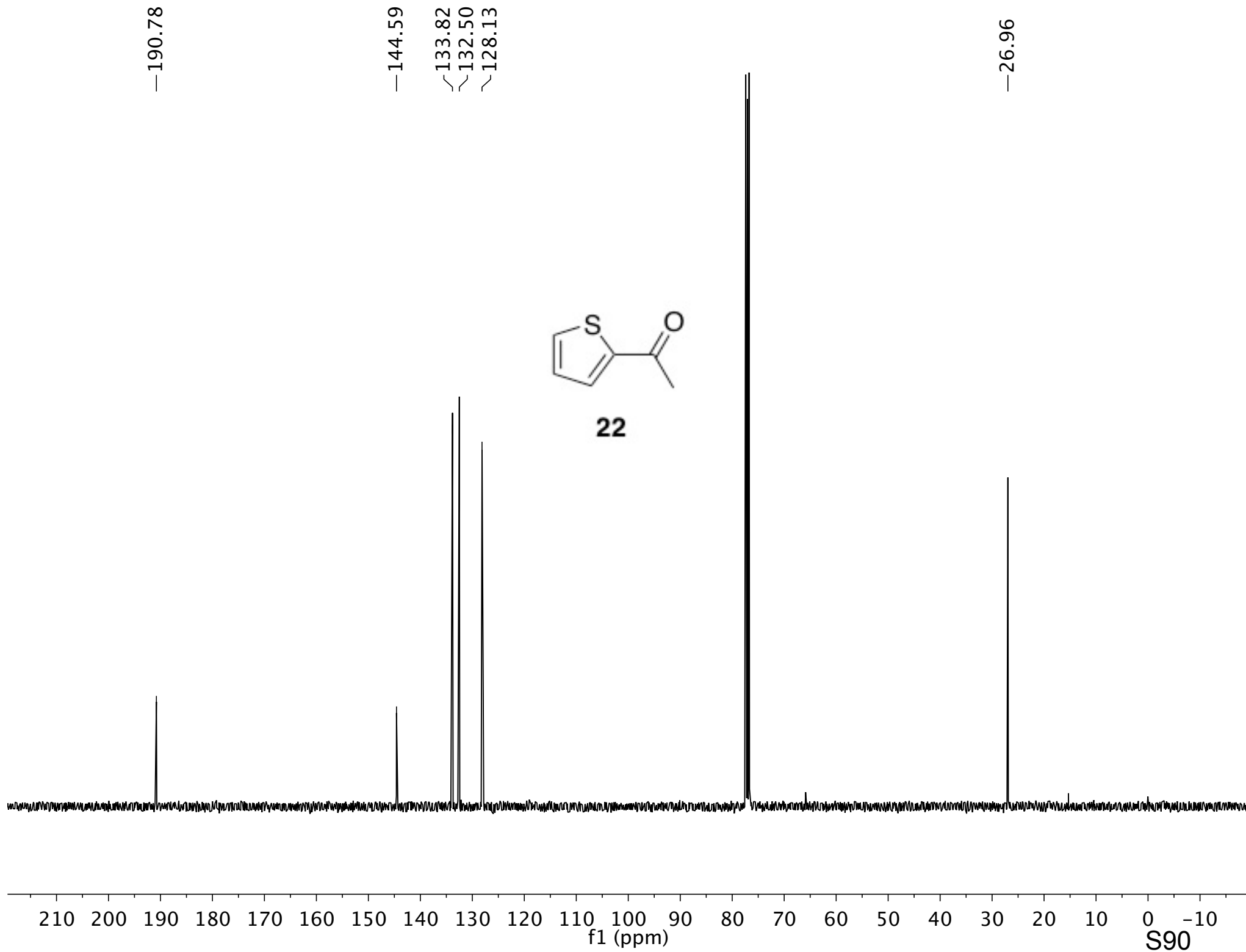
f1 (ppm)

S87



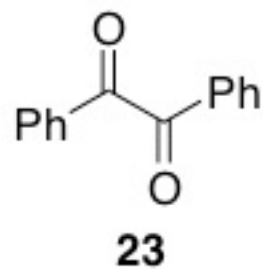






7.99  
7.99  
7.97  
7.97  
7.68  
7.66  
7.65  
7.54  
7.52  
7.50

4.00  
2.00  
4.01



H H H

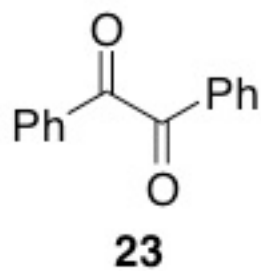
1.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

f1 (ppm)

S91

—194.60

134.92  
133.00  
129.94  
129.05

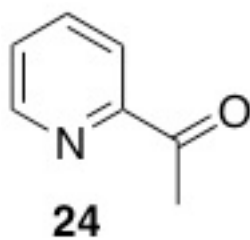


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10  
f1 (ppm)

S92

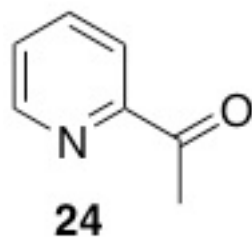
8.70  
8.69  
8.06  
8.06  
8.05  
8.04  
8.04  
8.03  
7.86  
7.85  
7.84  
7.83  
7.82  
7.82  
7.49  
7.49  
7.48  
7.48  
7.47  
7.47  
7.46  
7.46

1.00  
1.02  
1.02  
1.02



2.73  
3.17

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0  
f1 (ppm)  
S93



—200.28

—153.76

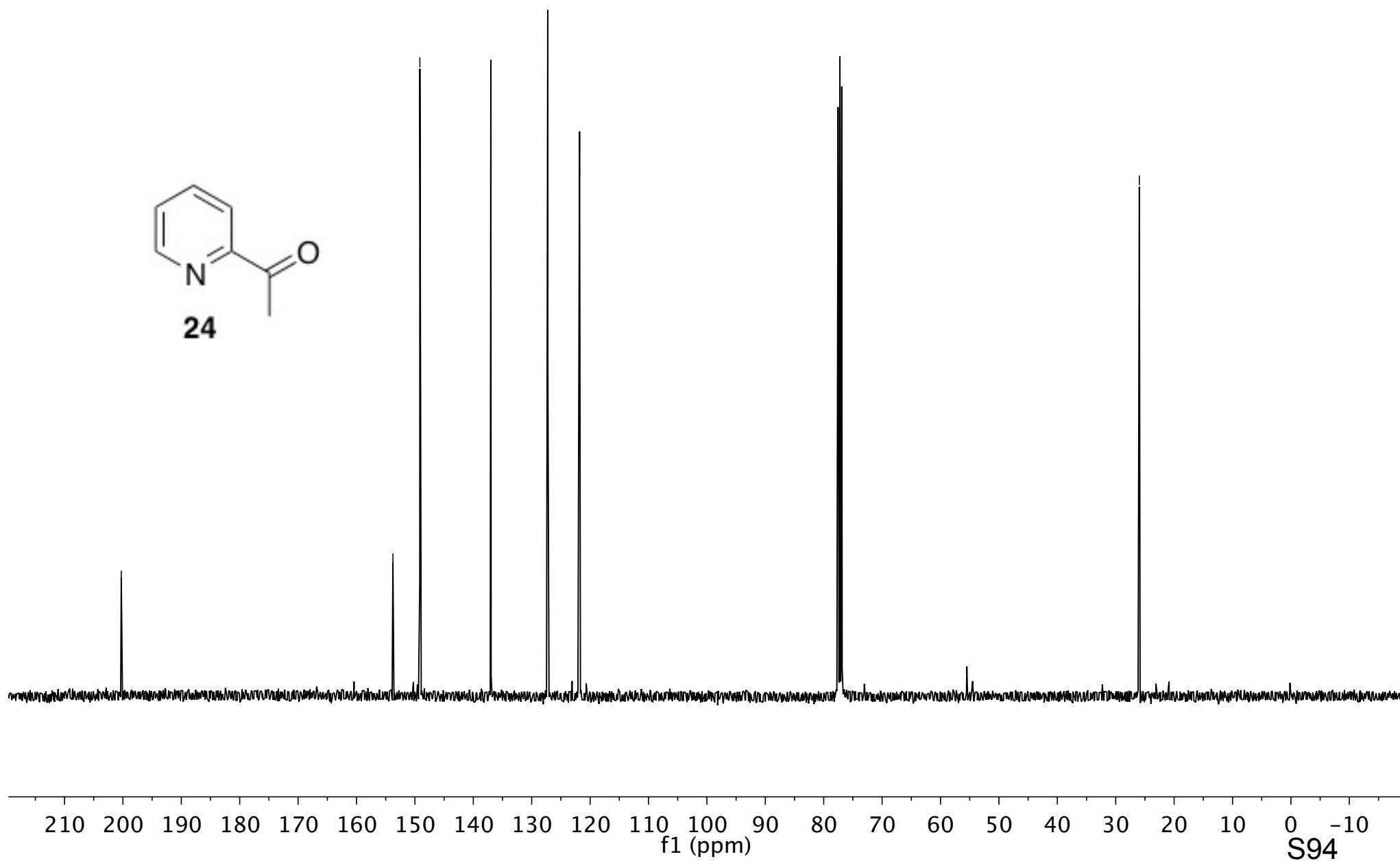
—149.15

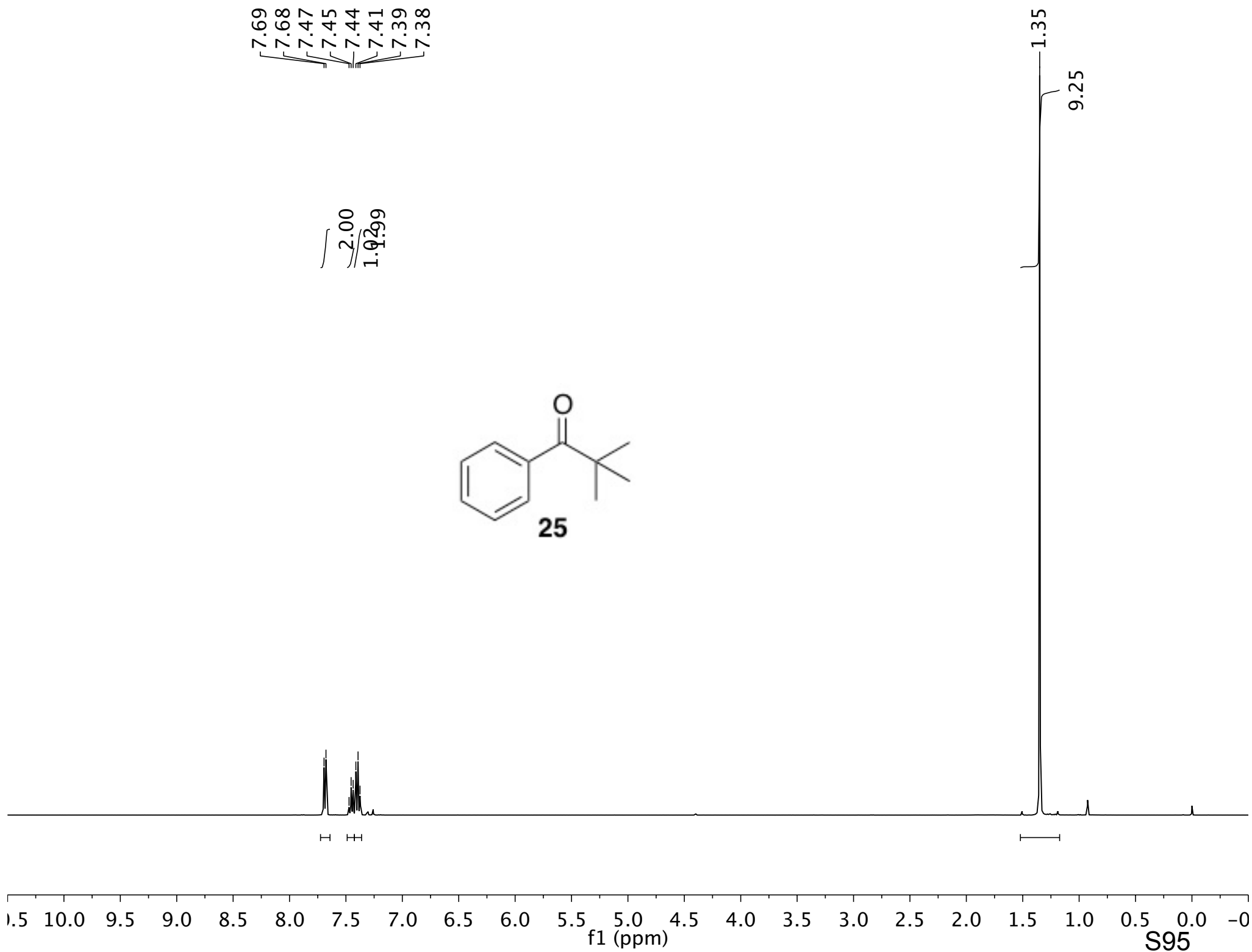
—137.00

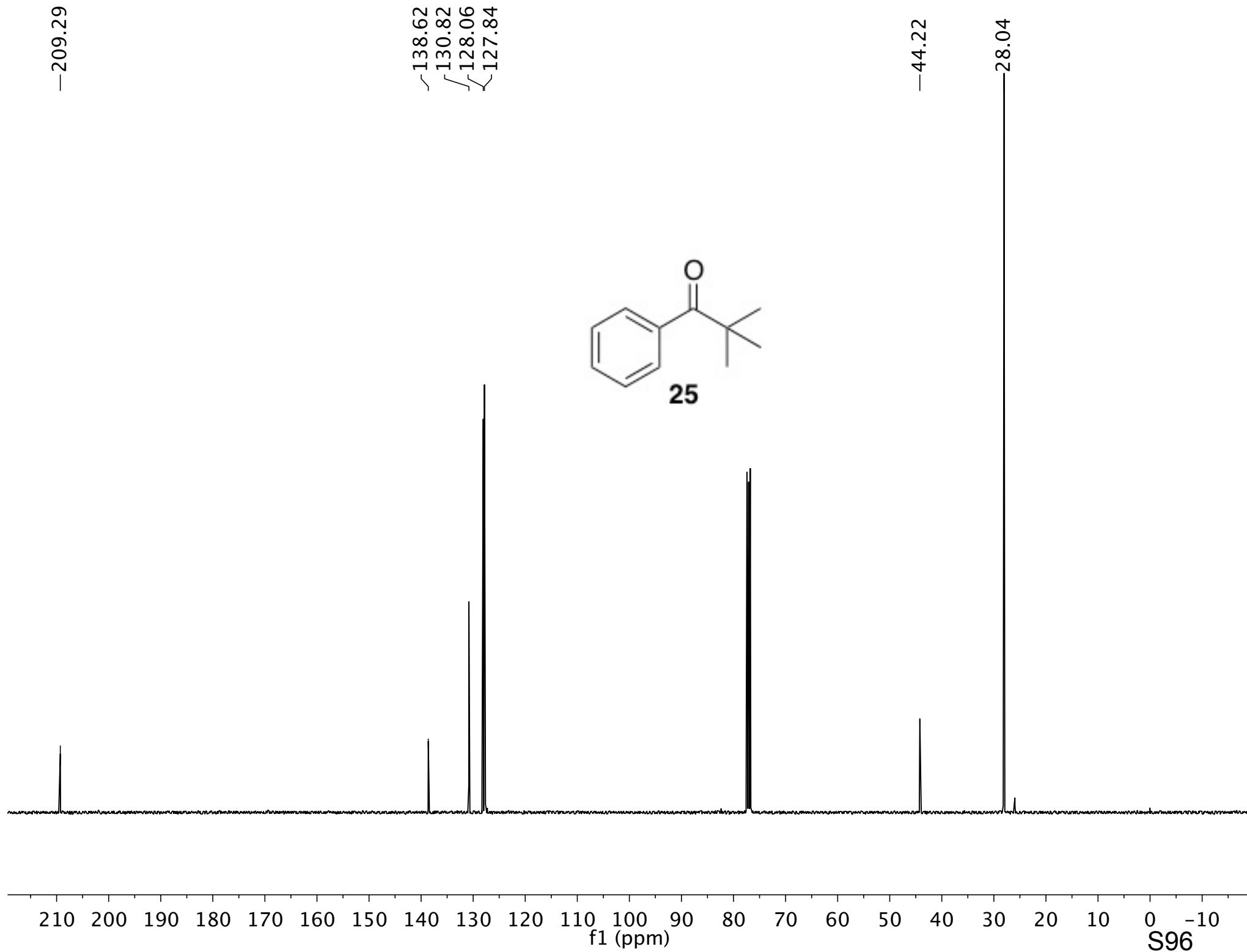
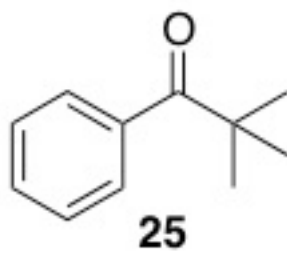
—127.25

—121.81

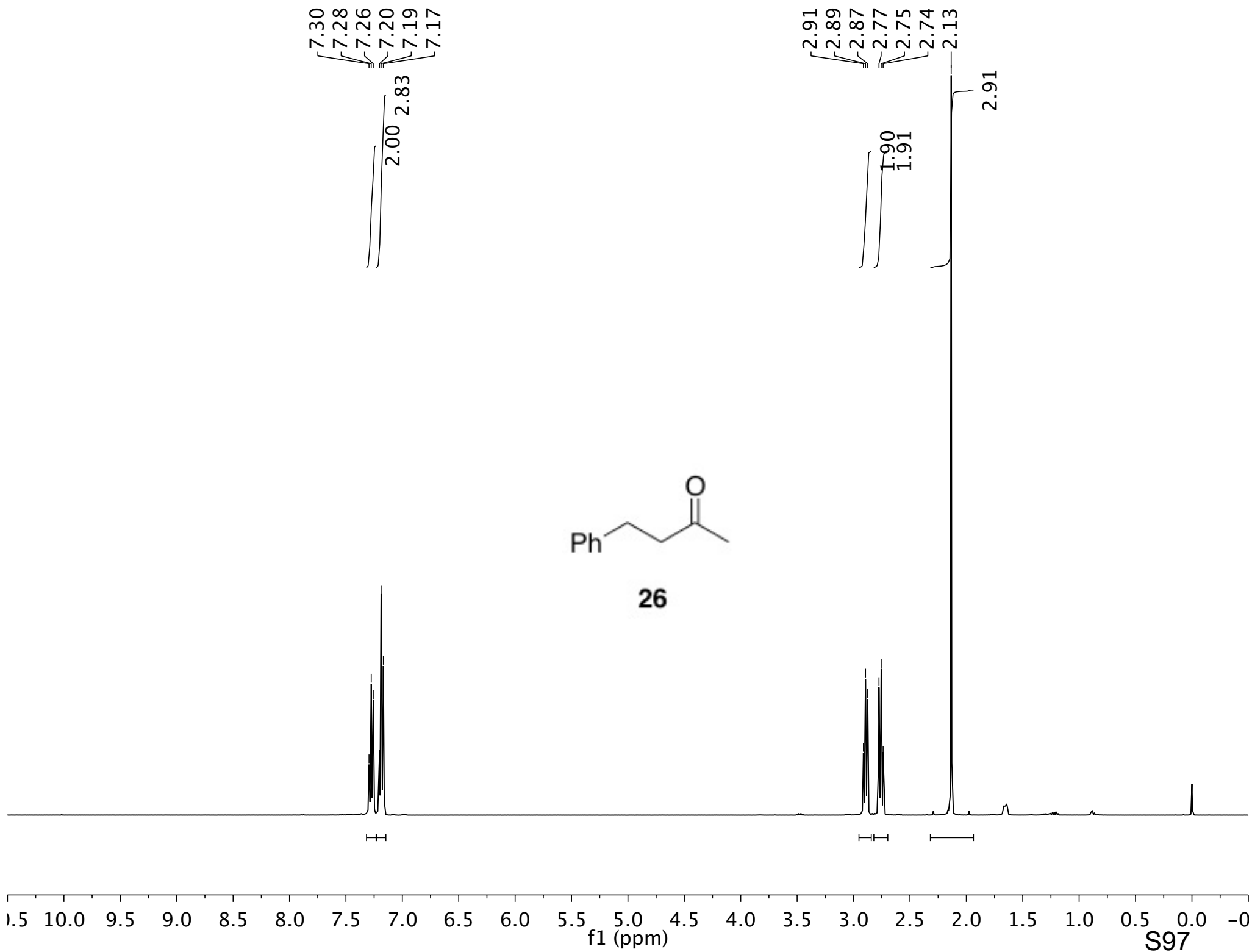
—25.96

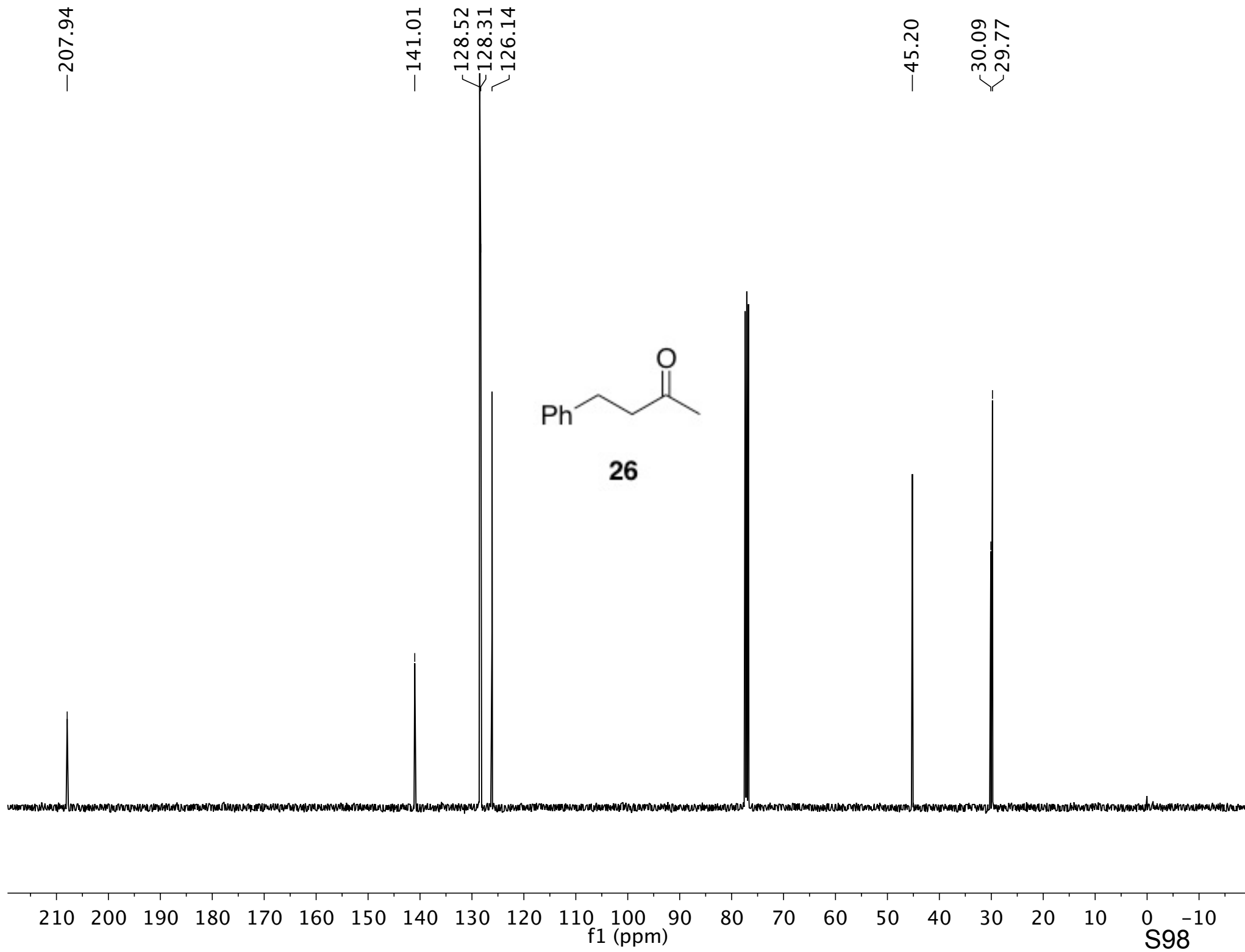


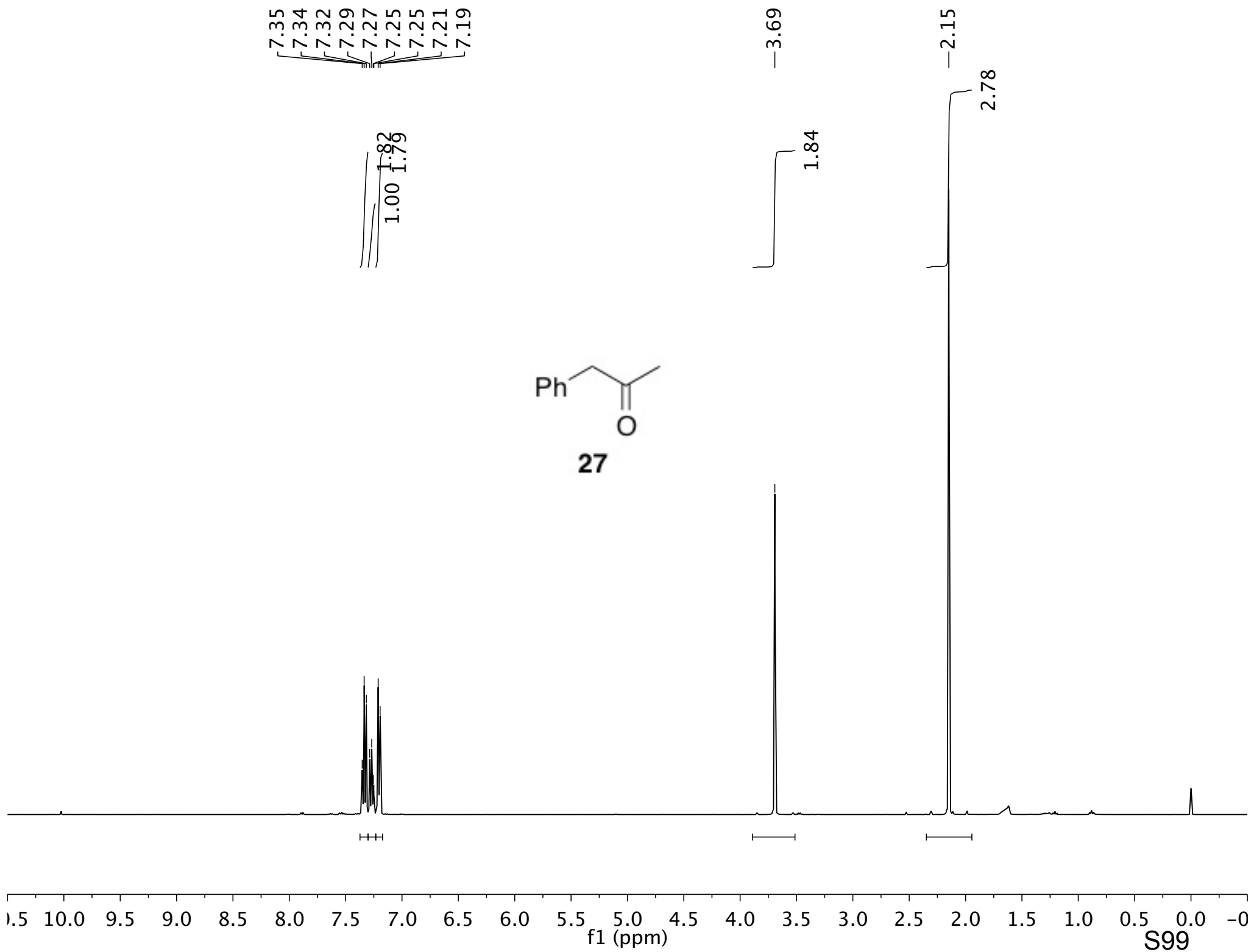


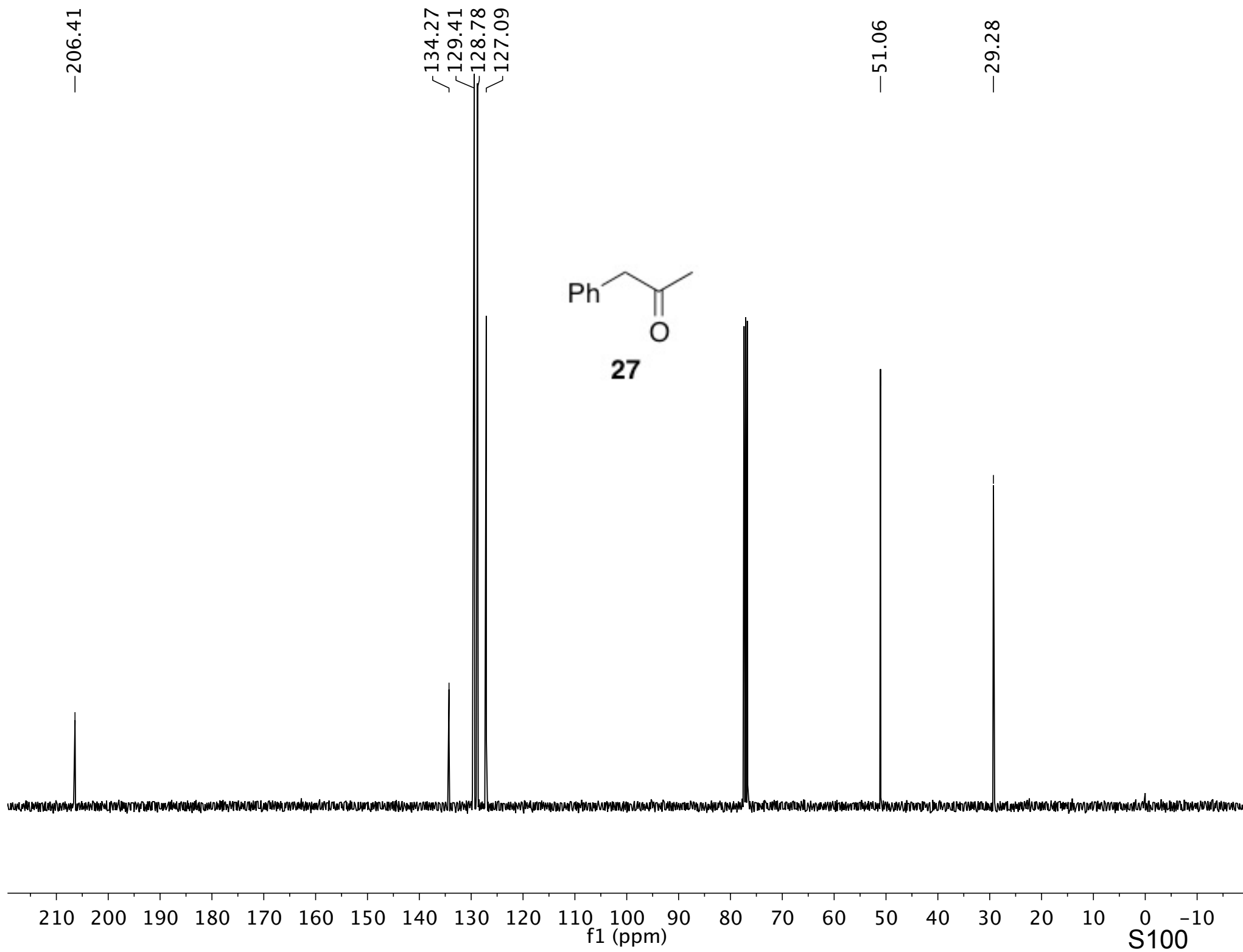


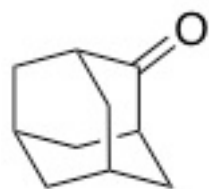




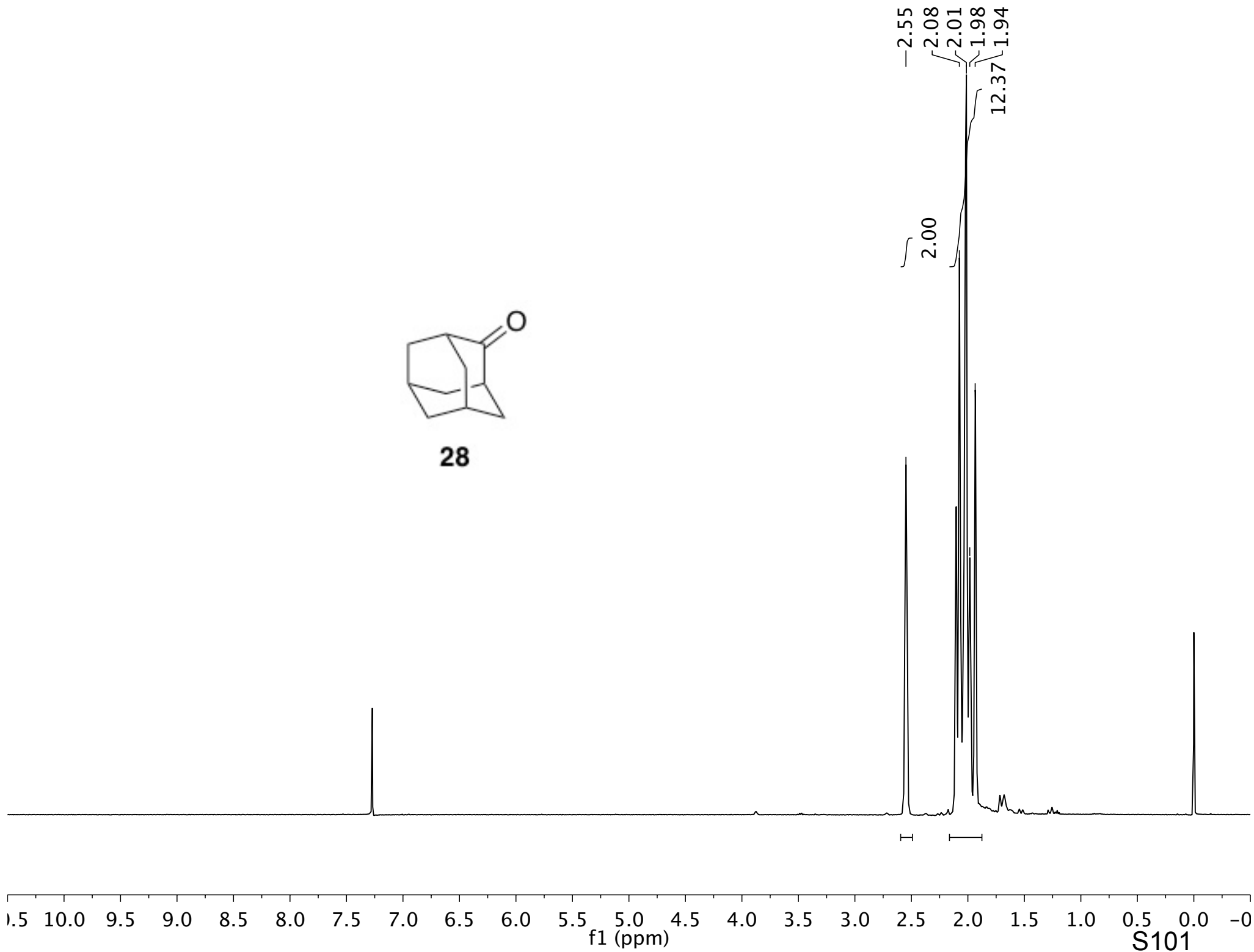


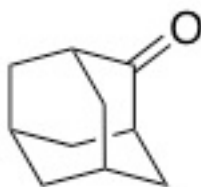




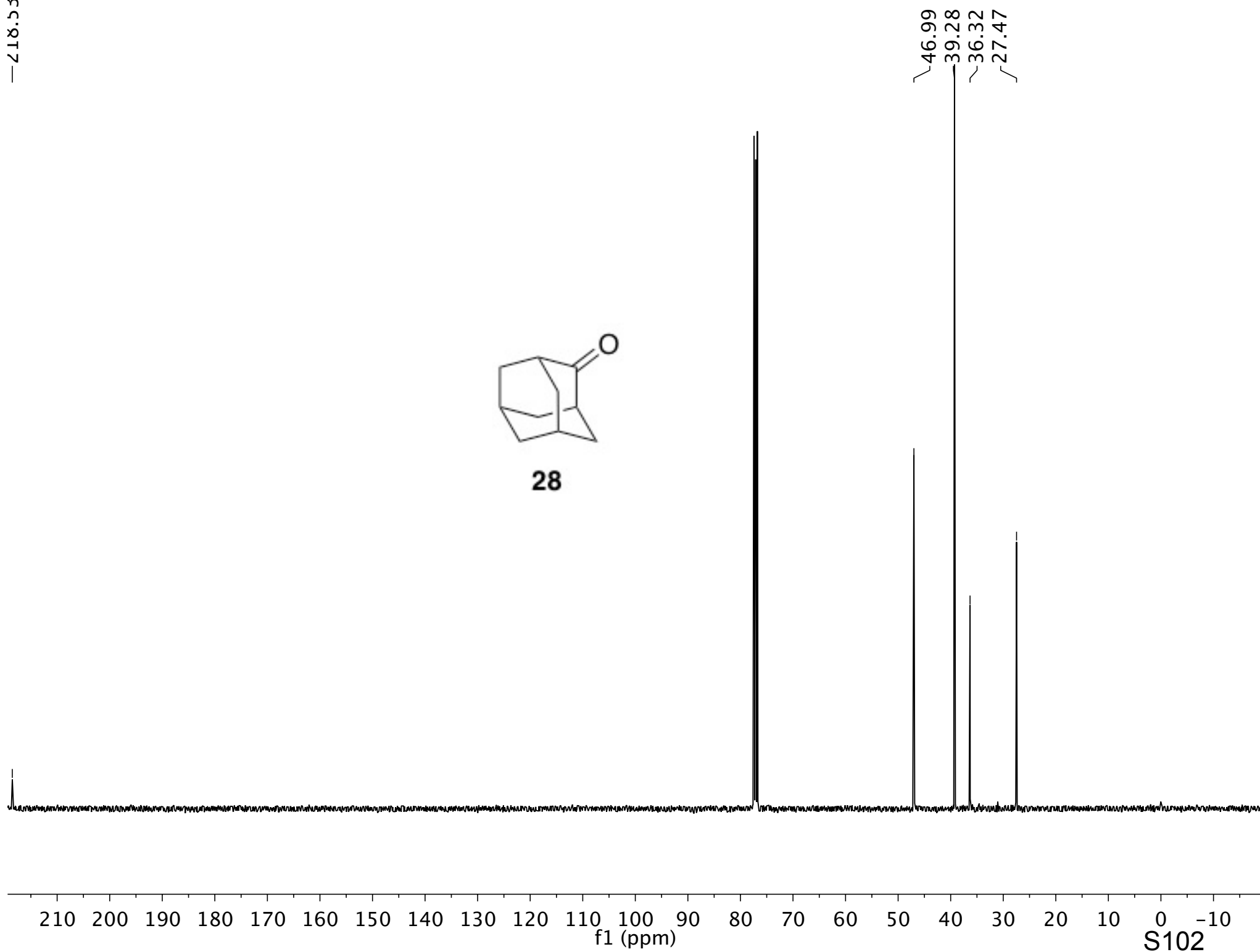


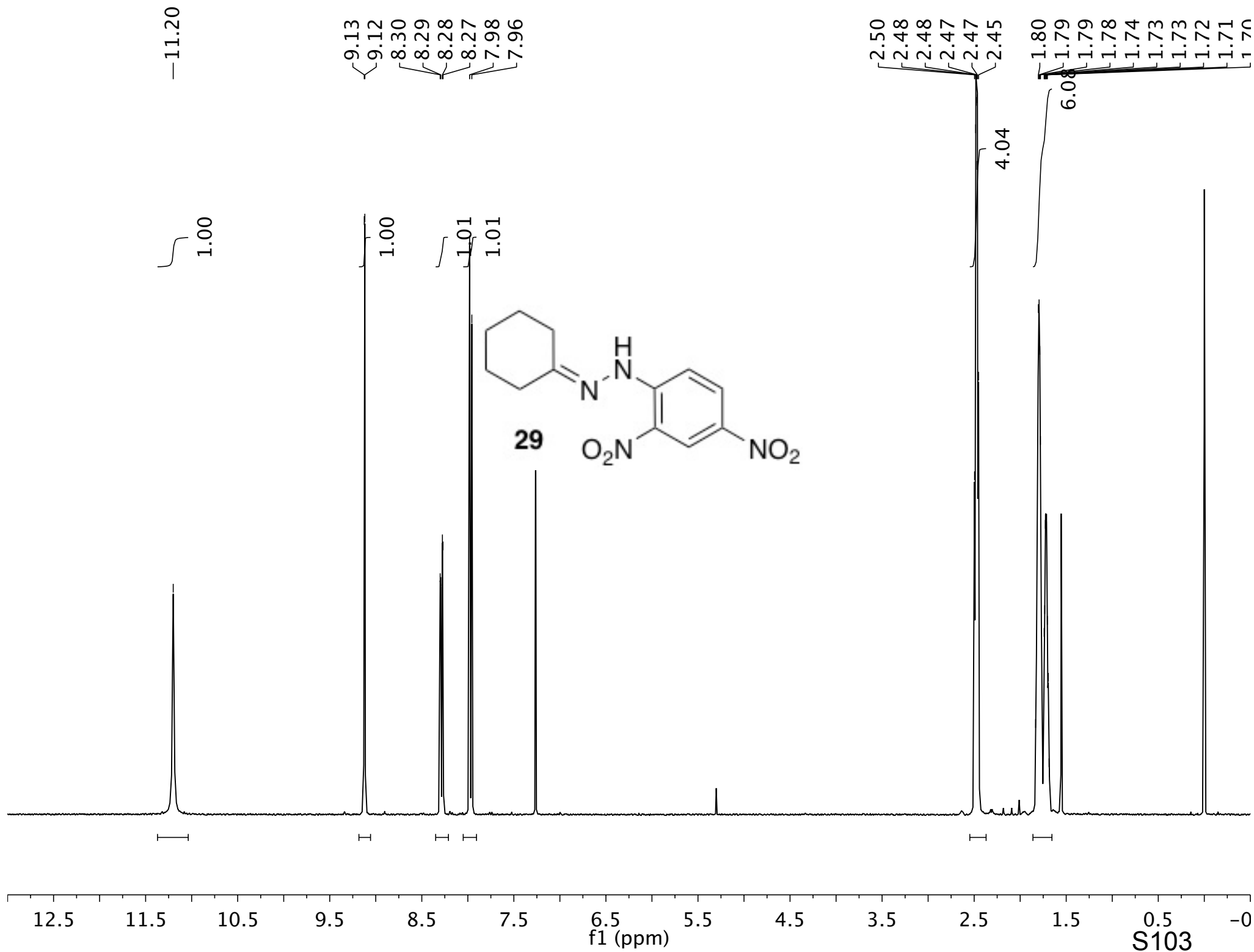
28

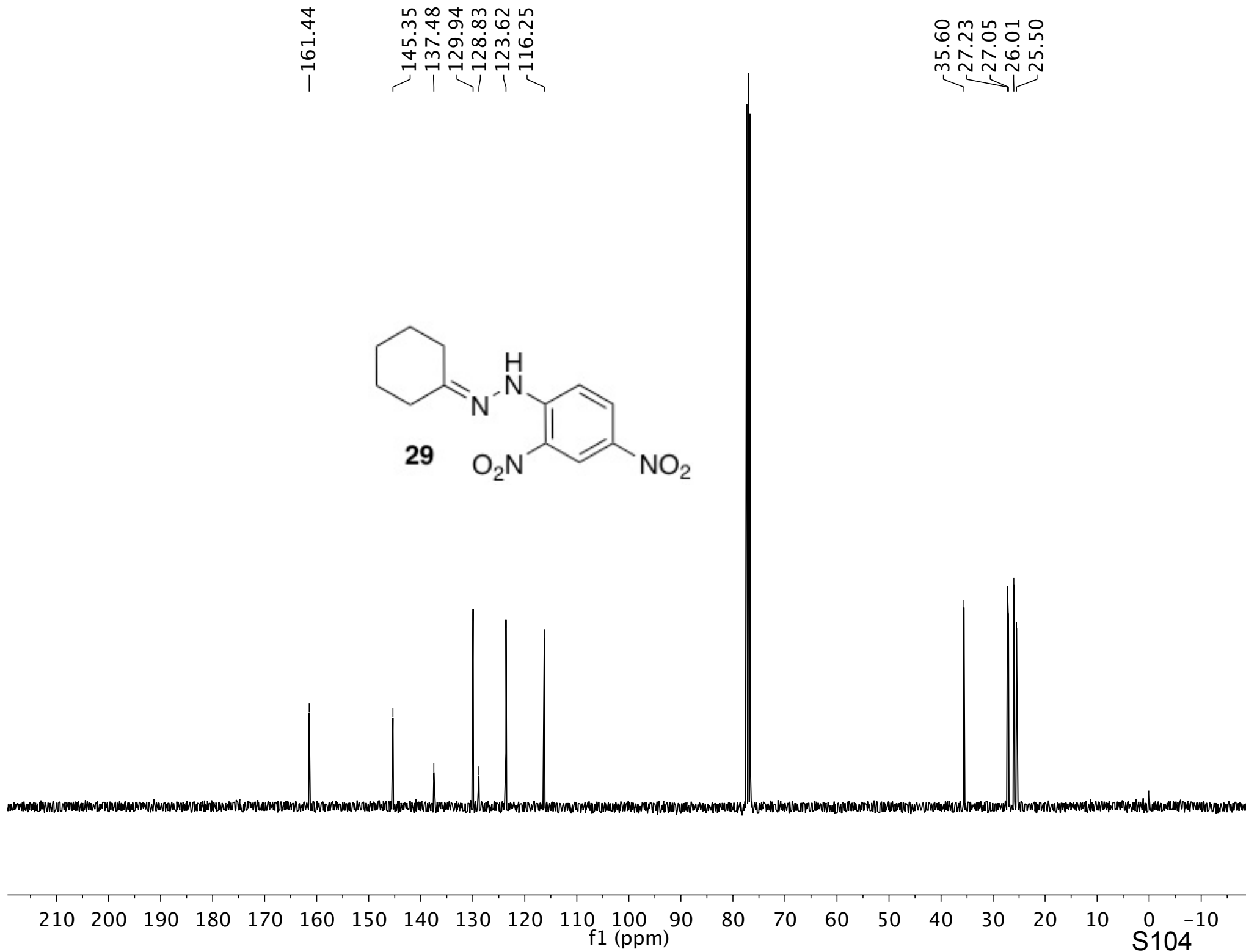




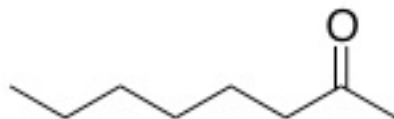
28



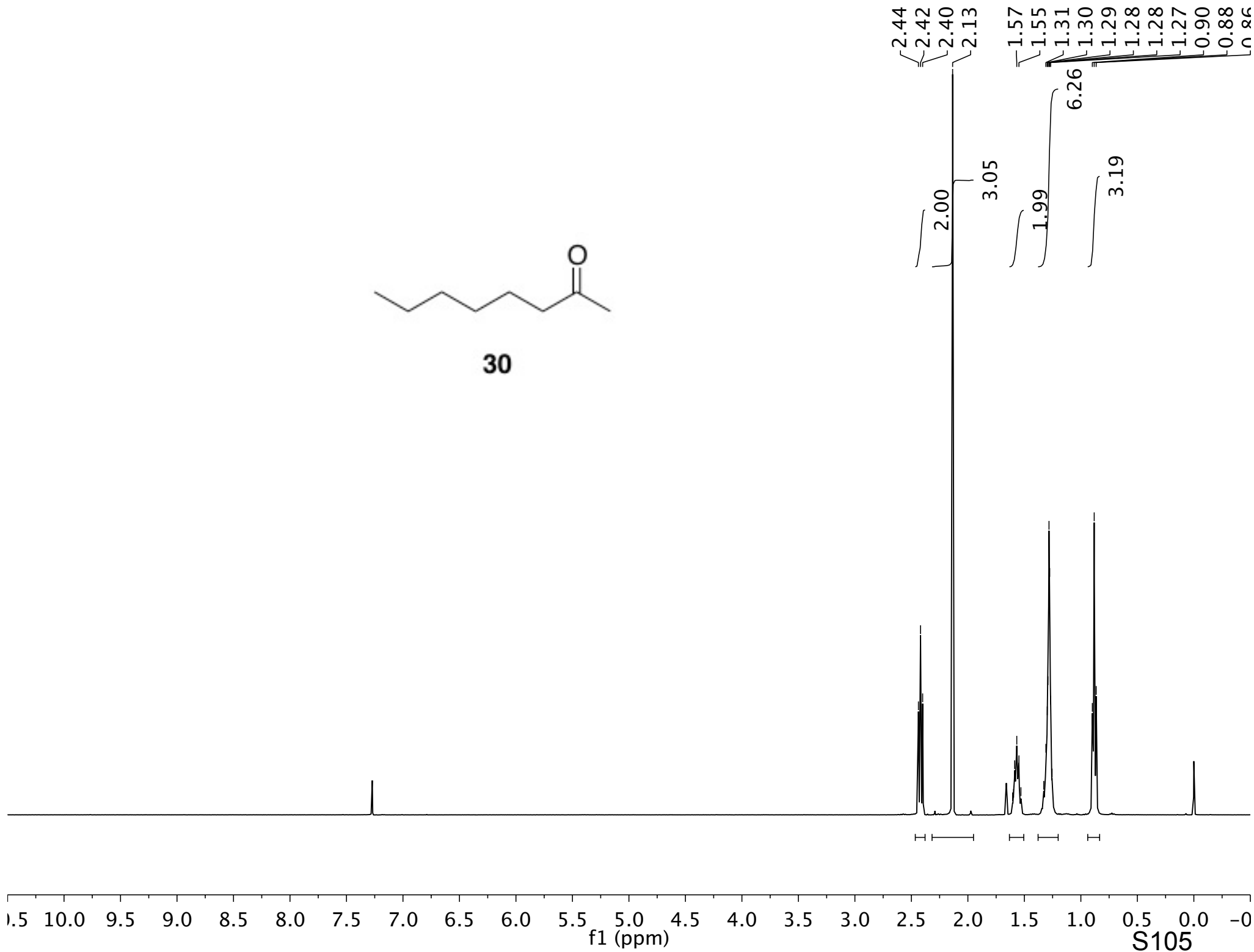








30



—209.42

—43.84

31.61

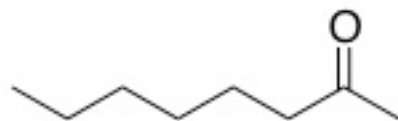
29.86

28.87

23.85

22.51

14.04

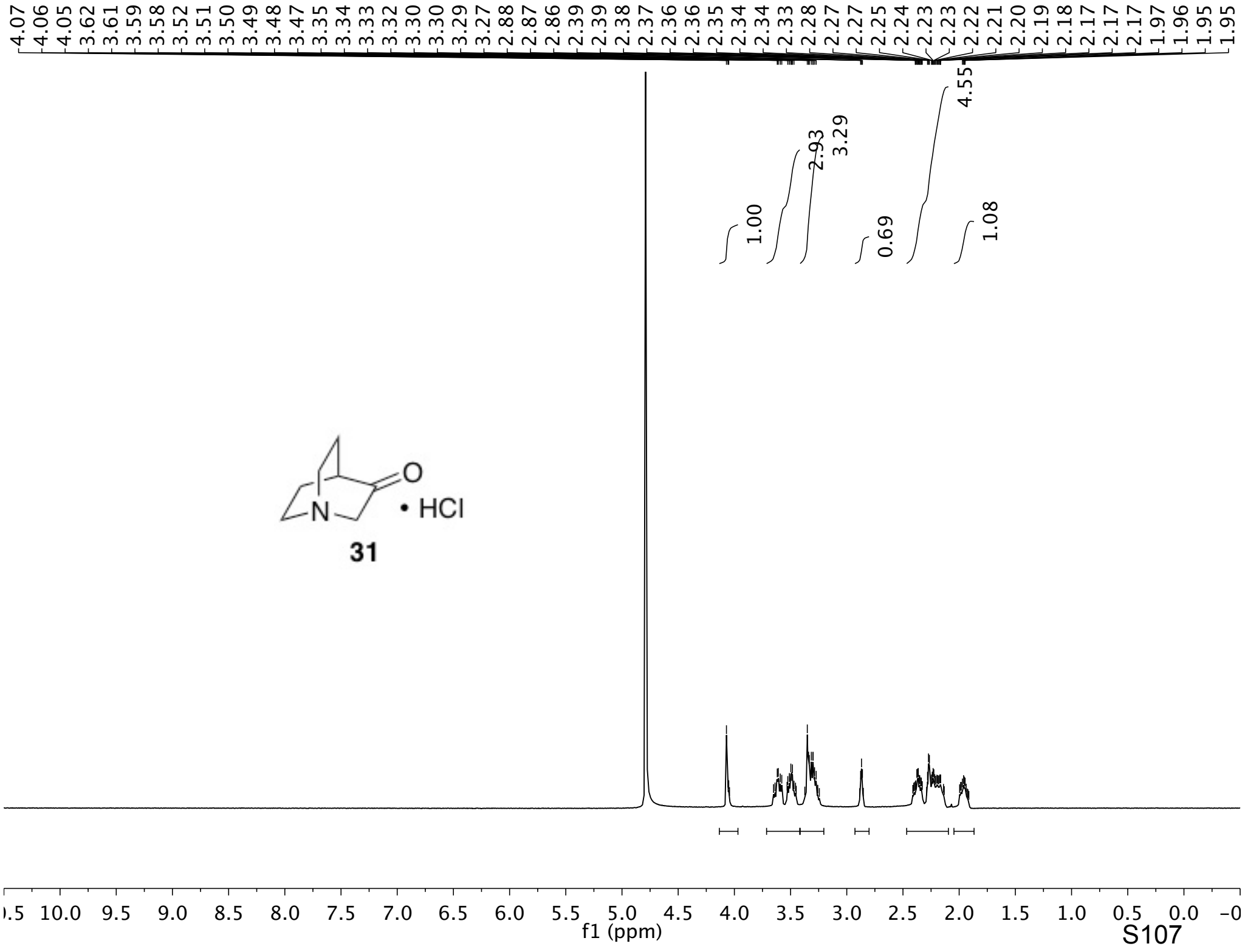
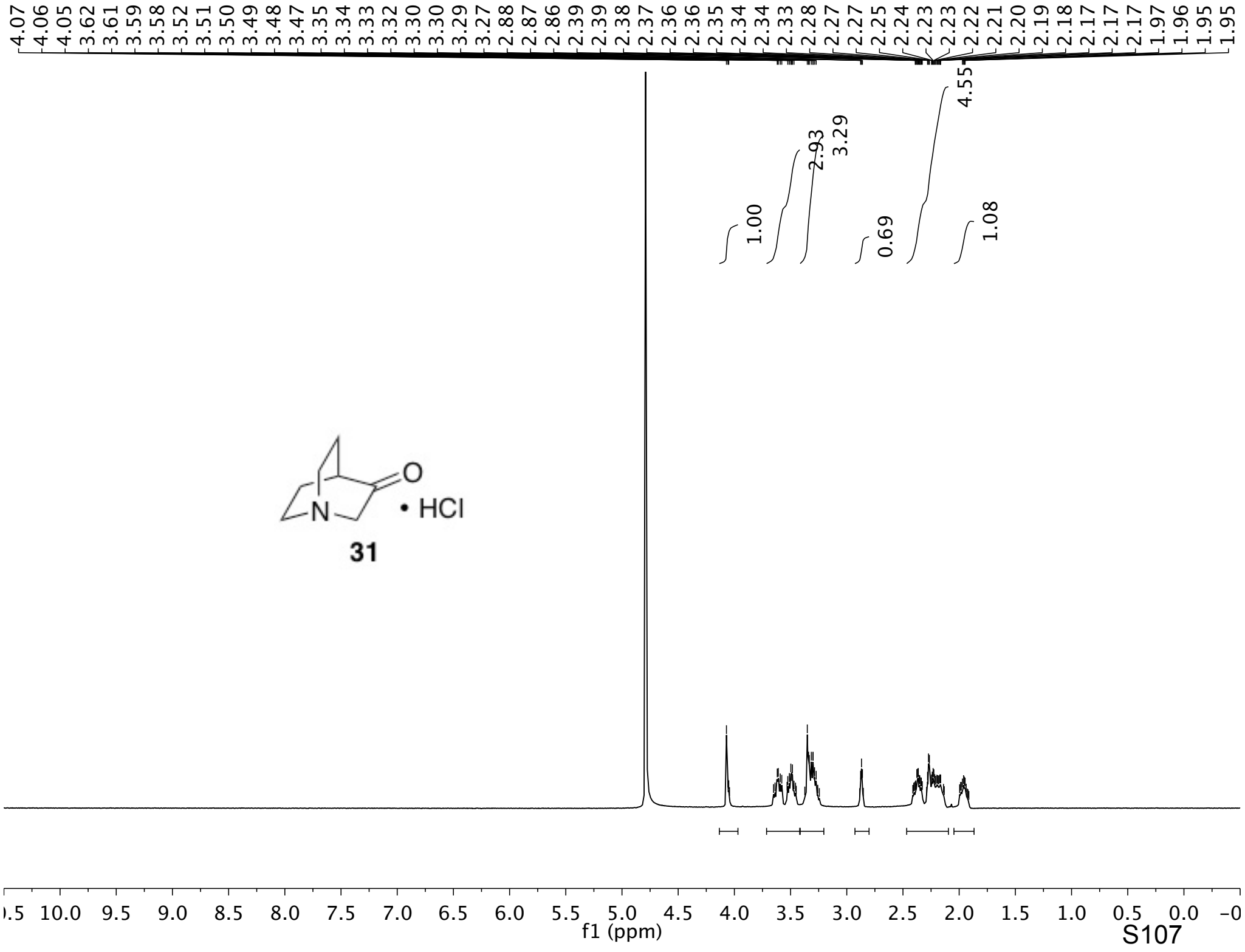


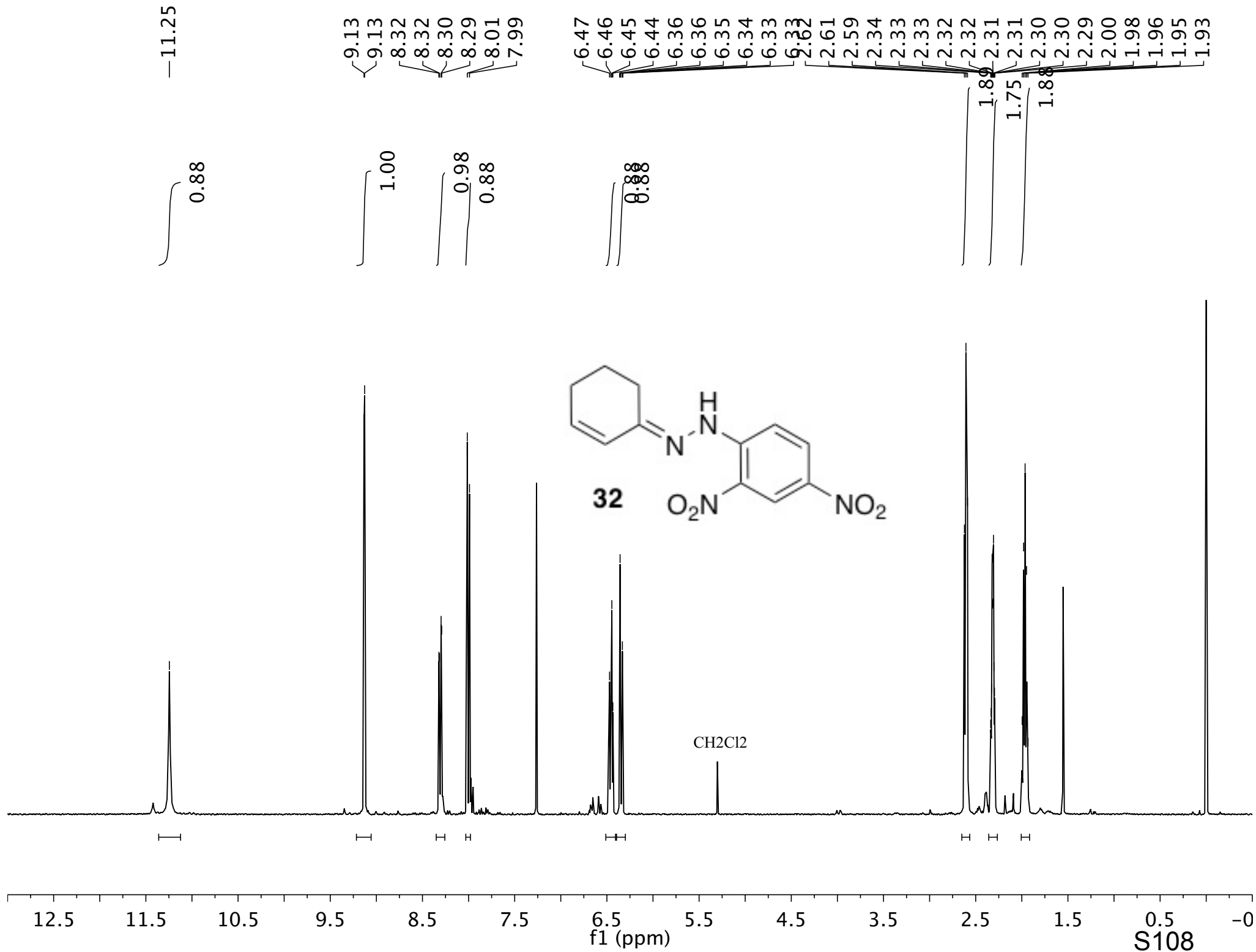
30

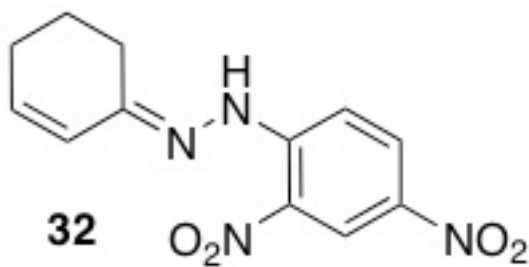
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

S106

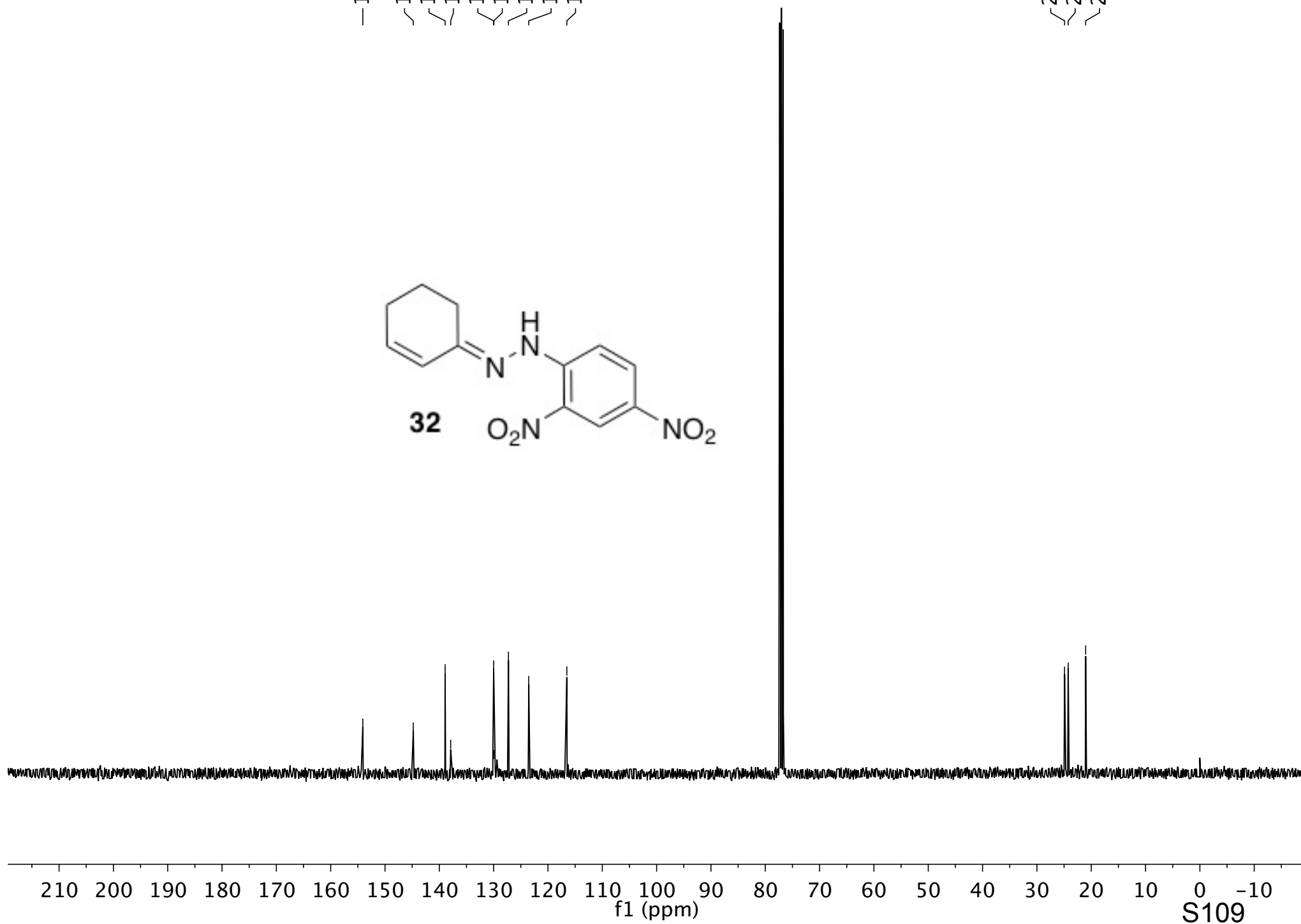


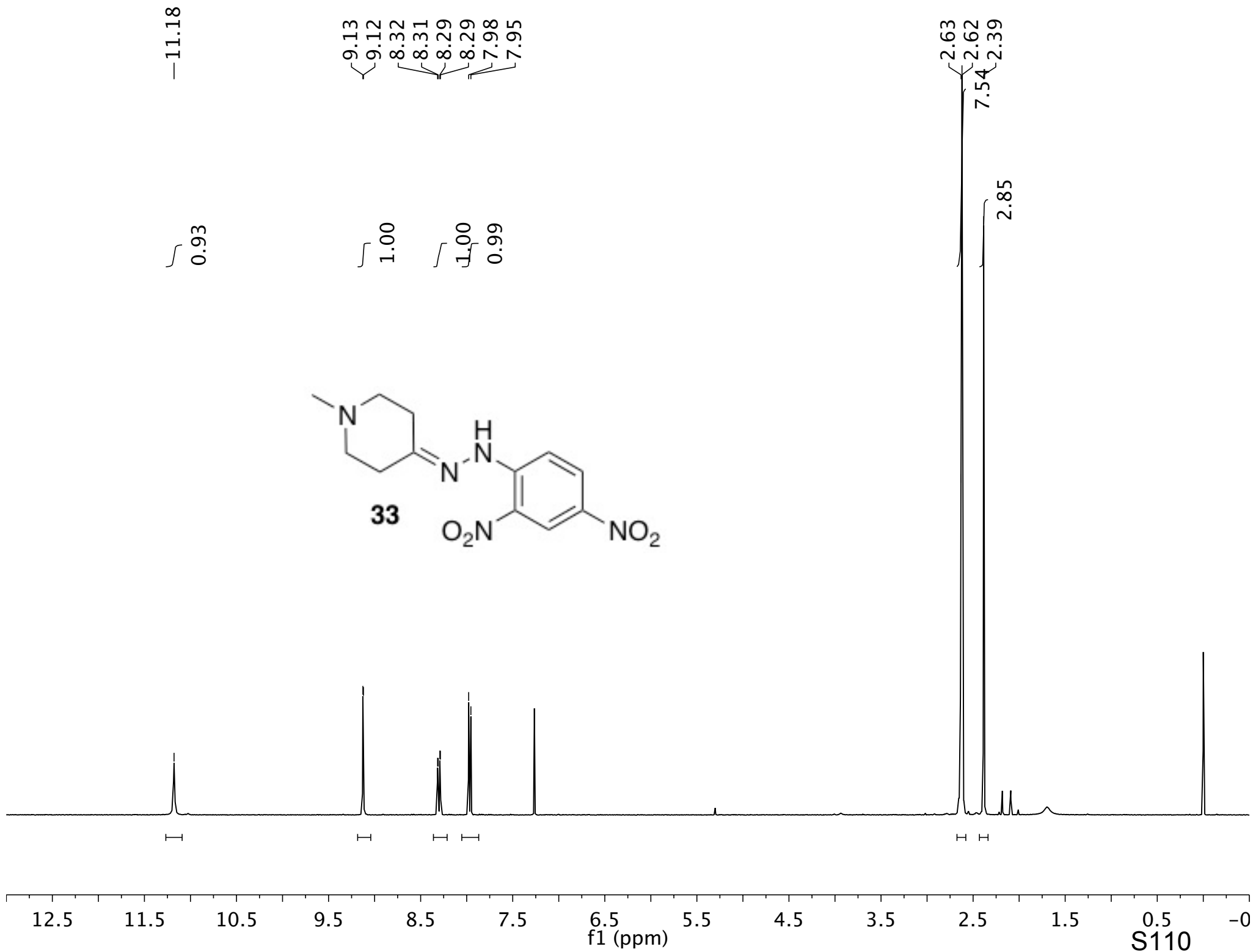


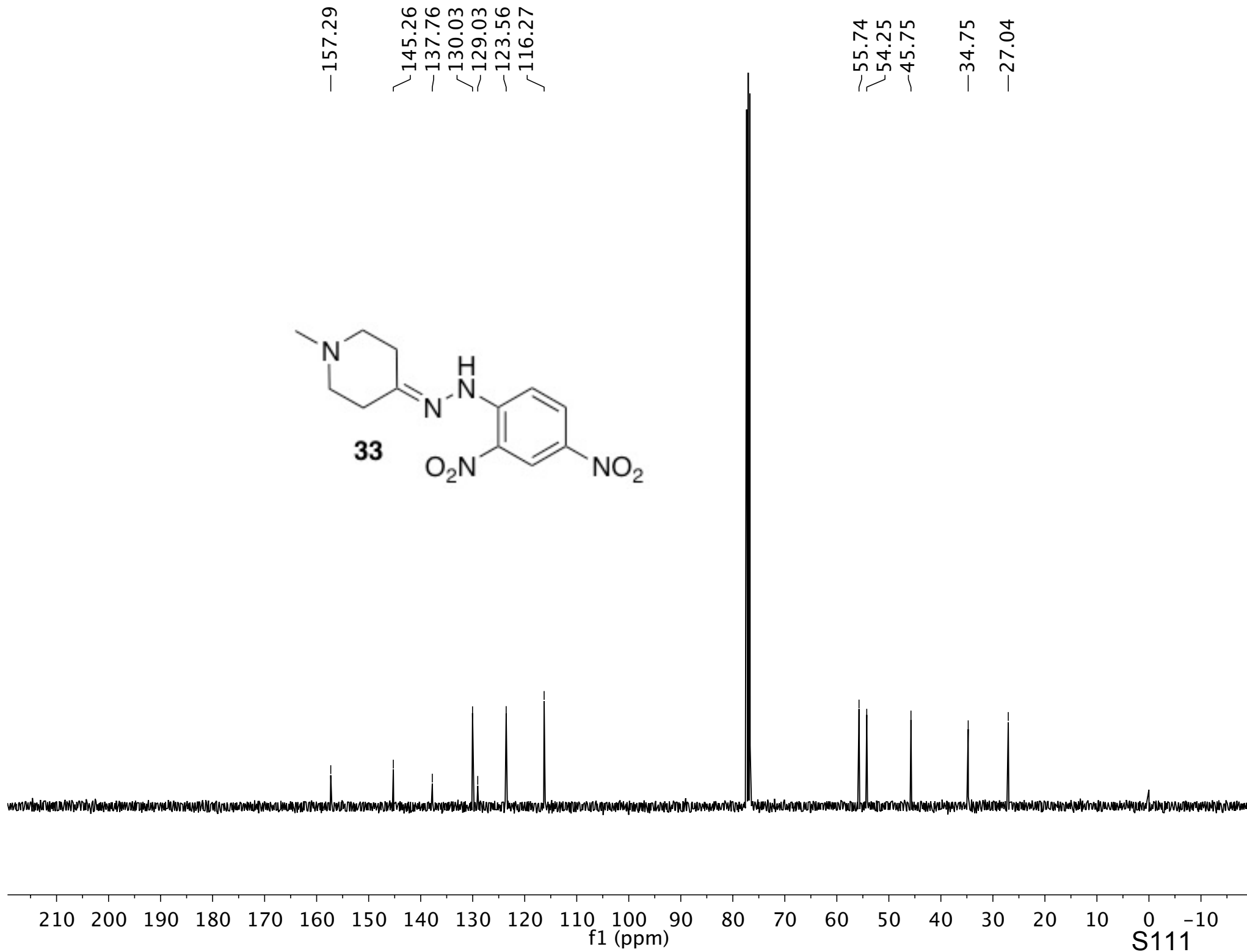
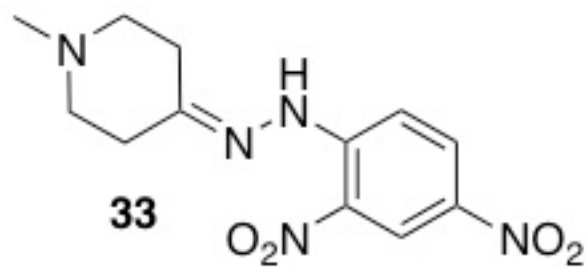


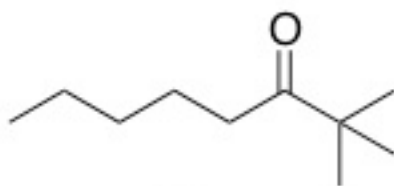
154.09  
144.79  
138.93  
137.91  
130.00  
129.97  
127.28  
123.54  
116.53

24.91  
24.24  
21.02

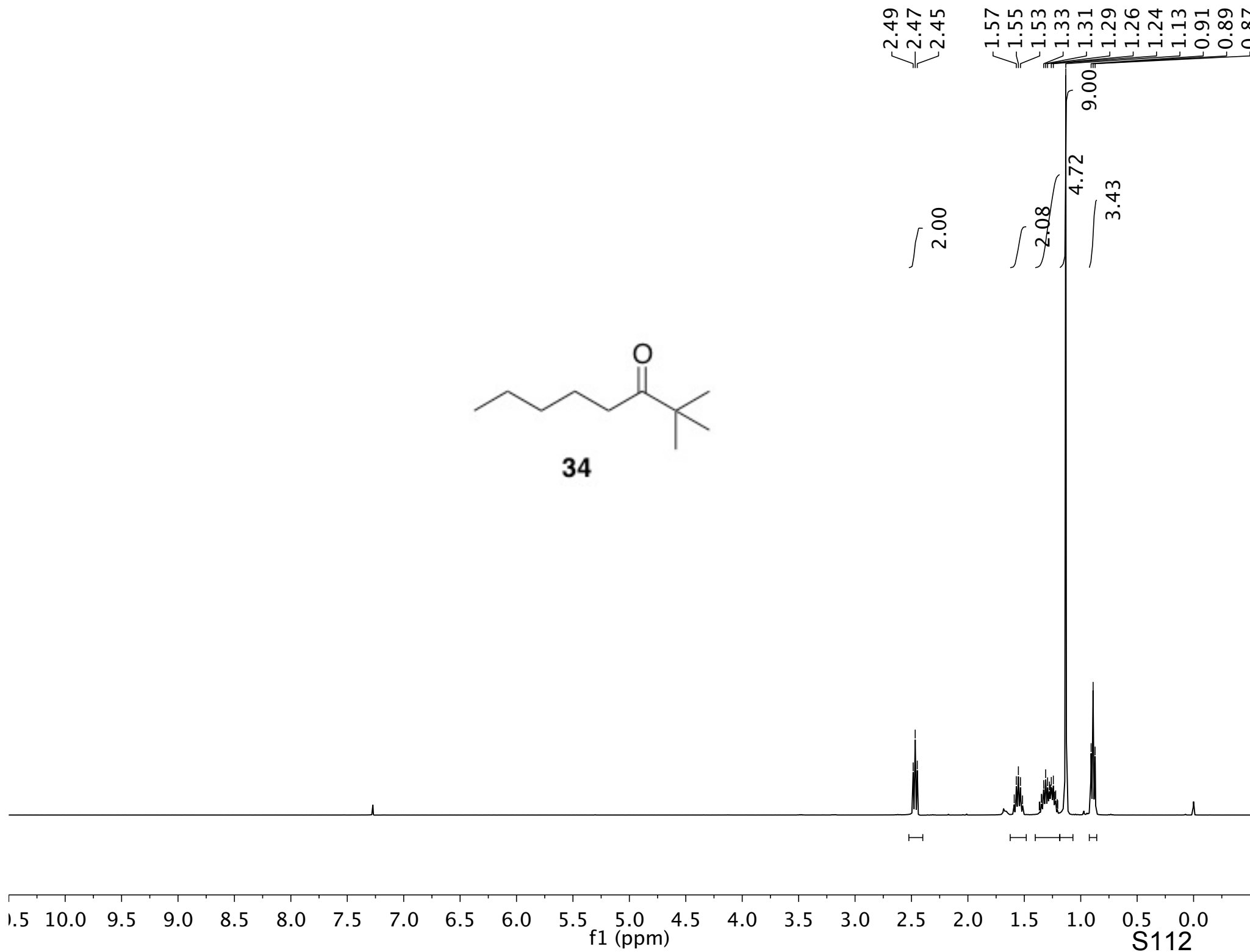






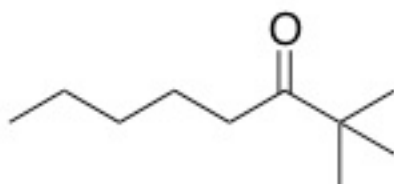


34



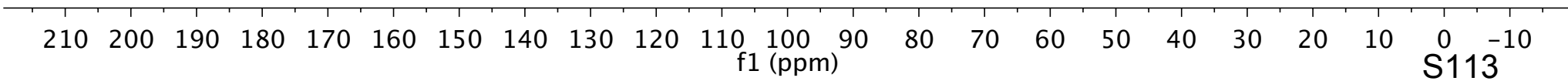


-216.14



34

44.09  
36.41  
31.53  
26.41  
23.64  
22.56  
13.96



S113

